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GROWTH AND CHARACTERIZATION OF ORGANIC STILABAZOLIUM SINGLE CRYSTAL OF N, N-DIMETHYLAMINO-N'-METHYLSTILBAZOLIUM P CHLOROBENZENESULFONATE (DASC) IN A MIXED SOLVENT SYSTEM

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ABSTRACT- Organic nonlinear optical crystal N, N-dimethylamino-N'-methylstilbazolium p-chlorobenzenesulfonate (DASC) has been successfully grown from mixed solvent of methanol:acetonitrile (1:1) solution by adopting slow solvent evaporation technique. Single crystal X-ray diffraction analysis was carried out and it shows that DASC crystal belongs to monoclinic structure with Cc space group. The optical absorption is studied by UV-Vis absorption spectra. Dielectric studies were also carried out for different temperature by varying the frequency.

Keywords- [Organic compound; X-ray diffraction; Stilbazolium derivative; nonlinear optical materials]

1. INTRODUCTION

During the last three decades, there has been intensive research efforts have been put in exploring and developing second order NLO materials for applications such as frequency conversion, electro optic modulation, optical parametric oscillation, parametric light generation and more recently, THz generation and detection. In this connection the THz emitting organic non-centrosymmetric nonlinear optical (NLO) crystals are attractive due to their superior NLO properties when compared to semiconductors and inorganic materials. Among organic NLO crystal, the popular ionic organic crystal 4-N,N-dimethylamino-4-methyl-stilbazolium tosylate (DAST) have made special attention. And now a day's THz spectrometers based on DAST crystal is available commercially. In DAST and its derivative crystal, the supramolecular interactions of ionic DAS analogous crystals are strong Coulombic interactions between the stilbazolium cation and benzenesulfonate anions. The π-π stacking interactions between cations and –S-O$^-$….H-C= interactions between the sulfonate group on anions and hydrogen atoms on cations makes this crystals has been potential crystal for NLO applications [1-2]. In this work we have

synthesized DAST derivative crystal of N,N-dimethylamino-N'-methylstilbazolium p-chlorobenzenesulfonate (DASC), which has DAST like structure and it is environmentally stable. We have made an attempt to grow bulk crystal in the mixed solvent system by slow solvent evaporation method. Here, the structural, optical and electrical properties of DASC single crystal have been investigated.

2. SYNTHESIS & CRYSTAL GROWTH

DASC was prepared by metathesization of the 4-N,N-dimethylamino-N'-methylstilbazolium iodide (DMSI) salt with sodium p-chlorobenzenesulfonate. DMSI was synthesized by the condensation of 1,4-dimethyl pyridinium iodide (2.35 g, 10 mmol), methanol (30 ml) and 4-N, N-dimethylamino-benzaldehyde (1.79 g, 10 mmol) in the presence of piperidine (0.2 ml). The total mixture was taken in a round-bottom flask and refluxed for 12 hours and cooled to room temperature. The product was filtered and recrystallized from methanol at least three times. The metathesizaton reaction was carried out as follows: Initially, 0.732 g (2 mmol) of DMSI was dissolved in 100 ml of distilled water by heating and simultaneously 0.4292 g (2 mmol) of sodium p-chlorobenzenesulfonate was dissolved in 30 ml of water with continued heating. These two hot solutions were mixed and further heated for 30 minutes at 70° C and then cooled to room temperature. The reaction resulted in the appearance of a red precipitate and the left out aqueous sodium iodide was separated from the former by vacuum filtration. The purity of DASC was further improved by successive recrystallization.

The crystal growth of DASC was a challenge since it dissolved well in various solvents but did not yield single crystal. It was speculated in this case that mixed solvent may provide a solution to this problem [3]. Crystal growth was performed by slow solvent evaporation technique. The solution was prepared with 2 g of DASC dissolved in 150 ml of mixed solvent of methanol and acetonitrile (1:1) at 35 ^{o} C in a constant temperature bath. After a period of 10 to 15 days time the single crystals were obtained and its showed in the figure 1.

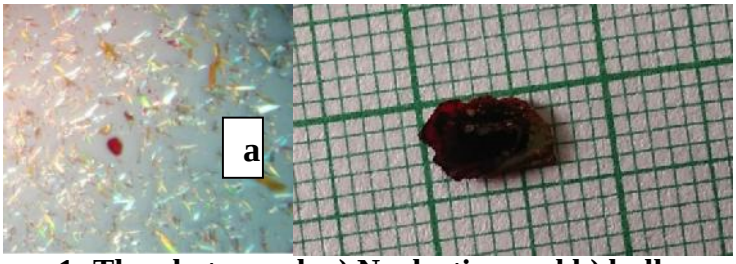

Figure 1- The photograph a) Nucleation and b) bulk grown DASC crystal

3. RESULTS& DISCUSSIONS

3.1. Single crystal X-ray diffraction analysis

The crystallographic structure of DASC was determined via single X-ray diffraction analysis using a Bruker Kappa APEX II diffractometer. The structure was determined from the single crystal XRD; it is found that DASC single crystal belongs to Monoclinic Crystal system, with the space group Cc. The unit cell parameters are a = 10.395Å, b = 11.201Å, c = 17.86 Å, α = 90 ^{o}, β= 92.06 ^{o}, γ = 90 ^{o}, Volume of 2081Å^{3}.

3.2. Optical absorption analysis

Figure 2 shows the absorption spectrum of DASC recorded in solid phase between the wavelength region 200 to2100 nm. Since the DASC crystal is iso-structural to DAST one may not expect much deviation in the optical absorption property. DASC indicates strong absorption upto 700 nm, it

correlating with the charge transfer process. This crystal is very transparent in higher wave lengths but at 1700 nm weak absorption observed for DASC crystal which is most probablydue to the overtones of the C-H stretching vibrations [4]. This crystal shows weak absorption at 700-1600 nm which makes the DASC is the potential crystal for NLO applications.

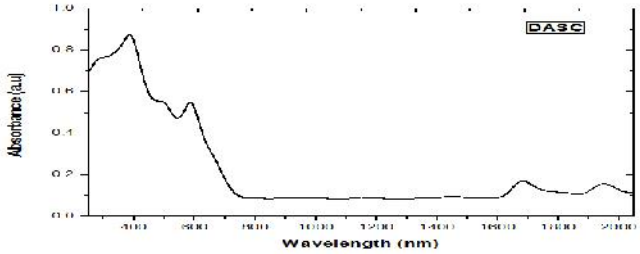

Figure 2- UV absorption spectrum of DASC crystal

4. DIELECTRIC STUDIES

The dielectric constant and dielectric loss of the DASC crystal were measured at different temperatures (313, 328, 348, 368 and 388 K) using a HIOKI 3532-50 LCR HITESTER in the frequency range 50 Hz to 5 MHz. The capacitance of the parallel plate capacitor with DASC sample kept as dielectric medium at different temperatures (308,328, 348 and 368 K) was measured. The dielectric constant (ε_r) was calculated using the relation:

$$\varepsilon_r = \frac{Cd}{\varepsilon_0 A}$$

Where, C the capacitance, d the thickness of the sample, ε_0 the permittivity of free space and A the area of the crystal. Fig.3a shows the variation of dielectric constant as a function of frequency at different temperatures. It is observed that the value of dielectric constant decreases with frequency and becomes almost constant at higher frequency. The observed low dielectric constant at higher frequency may due to the loss of significance of all these polarizations gradually. Fig. 3b illustrates the variation of dielectric loss as a function of both the applied frequency and temperature. The sample shows large dielectric loss at low frequencies. The dielectric loss decreases with increase in frequency at almost all temperatures. The larger value of dielectric loss at low frequencies can be ascribed to the space charge polarization due to charged lattice defect [6]. The low value of dielectric constant at higher frequencies is significant for the fabrication of materials for photonics and electro-optic devices.

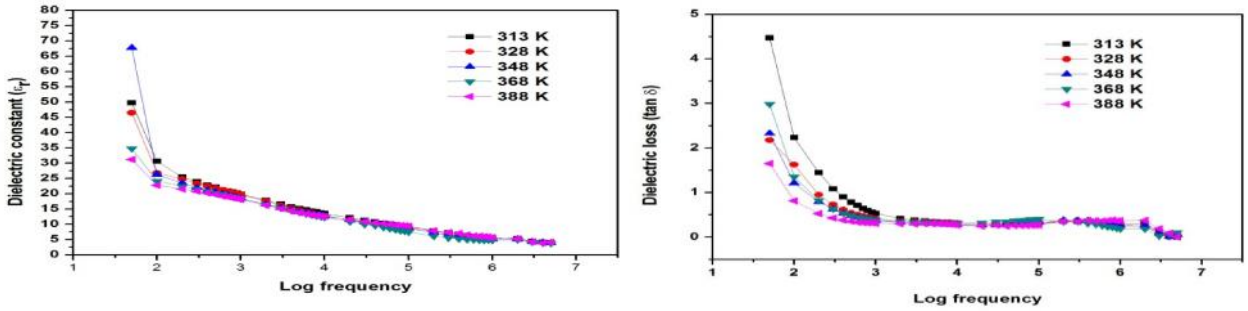

Figure 3- Frequency dependence of a) dielectric constant and b) dielectric loss of DASC crystal

CONCLUSION

An efficient stilbazolium derivative crystal of DASC was successfully grown by slow evaporation technique in a mixed solvent system. The single crystal X-ray diffraction analysis confirmed the noncentrosymmetric space group and the monoclinic structure. The optical absorption property was found for the developed material. Dielectric measurements in the frequency range of 50 Hz - 5 MHz suggest that the permittivity and the dielectric loss of DASC decrease with increase in frequency at different temperatures.

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