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High-Quality Crystal Growth and Characterization of Organic Nonlinear Optical Crystal Dast

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Abstract: The growth and characterization of a highly nonlinear optical 4-N,N-dimethylamino -4'-N'-methyl stilbazoliumtosylate (DAST) crystal is reported by adopting slope nucleation coupled with slow evaporation method. Parallel glass platesare used as slopes for the growth of crystals. The structure and composition of the grown crystal are studied by single crystal X-ray diffraction and CHN analysis. FTIR spectrum of the crystal confirms the presence of various functional groups. UV- vis -NIR spectral analysis is used to know the optical quality of the grown crystal. Thermal behavior of DAST is investigated using thermo gravimetric analysis (TGA). Mechanical strength is analyzed using Vicker's Micro hardness test.
Keywords: Crystal growth, Slow evaporation, Single crystal XRD,FTIR ,Microhardness.

1. Introduction and Experimental:

Ionic organic materials are advantageous among the various classes of NLO materials, due to their preferred mechanical, chemical and thermal properties [1]. DAST is one of the technologically important ionic organic crystals with large EO and NLO coefficients and used to produce THz waves [2]. As the DAST crystal is the best organic THz emitter, in the present study, an attempt has been made to grow a good quality single crystal of DAST by adopting the parallel plate slope nucleation method and by slow evaporation of the solvent.

DAST was synthesized by the condensation of 4-methyl-N-methyl pyridiniumtosylate, which was prepared from 4-picoline and methyl p-toluene sulphonate and 4- dimethylaminobenzaldehyde in the presence of piperidine [3]. The product was purified by successive recrystallization from methanol.

The DAST–methanol supersaturated solution was prepared from the solubility data of DAST.4g of DAST was dissolved in 400 mL of methanol andwas taken in a 500mL Teflon beaker. The solution was stirred for 1 h at 45 °C to ensure homogeneity. After this a set of parallel plates made of glass with 2 mm gap was inserted in the beaker in slanting position. The beaker was kept at room temperature for slow evopration. DAST crystals of size 15x8x0.6 mm^3 were grown in three weeks' time.

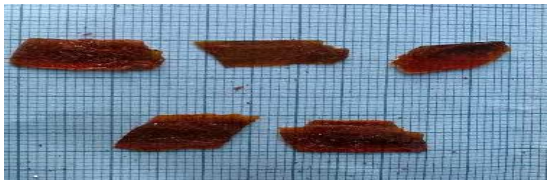

Fig.1.Photograph of DAST single crystals

2. Results and Discussion

Single crystal X-ray diffraction was analysed using ENRAF NONIUS CAD-4 diffractrometer. Single crystal X-ray diffractometry analysis revealed that DAST crystal belongs to the monoclinic system with space group Cc. The cell parameters values are a=10.572Å, b= 11.331 Å and c=17.523 Å and $\alpha=\gamma=90$, $\beta=91.32$ and Volume = 2098.54($Å^3$). The elemental composition of the grown DAST crystal was carried out by CHN analysis. The calculated values of $C_{23}H_{26}N_2O_3S$ are: C= 67.27%, H= 6.38% and N=6.85% and the corresponding experimentally found values are: C= 67.49%, H = 6.75% andN=6.71%.

The FTIR spectrum for DAST crystal was recorded in the wavelength range 500 to 4000 cm^{-1}. In Fig. 2, the peak at 3015 cm^{-1} is assigned to the aromatic C-H stretch. The peak at 2902 cm^{-1} is assigned to the CH_3asymmetric stretch. The peaks at 1575cm^{-1} and 1518 cm^{-1} are attributed to the aromatic ring vibrations. The peak at 1361 cm^{-1} corresponds to CH_2 bending and C-N stretching mode. The peak at 807 cm^{-1} is assigned to the 1, 4 distributed aromatic ring. The in-plane and out-plane deformations bands are observed at 1510 $cm^{-1}$and 750 cm^{-1} respectively. The spectrum further shows that the bands in the range 3492 cm^{-1} to 2627 cm^{-1} are relatively less intense, suggesting that the grown crystal is an ordered single crystal in nature .

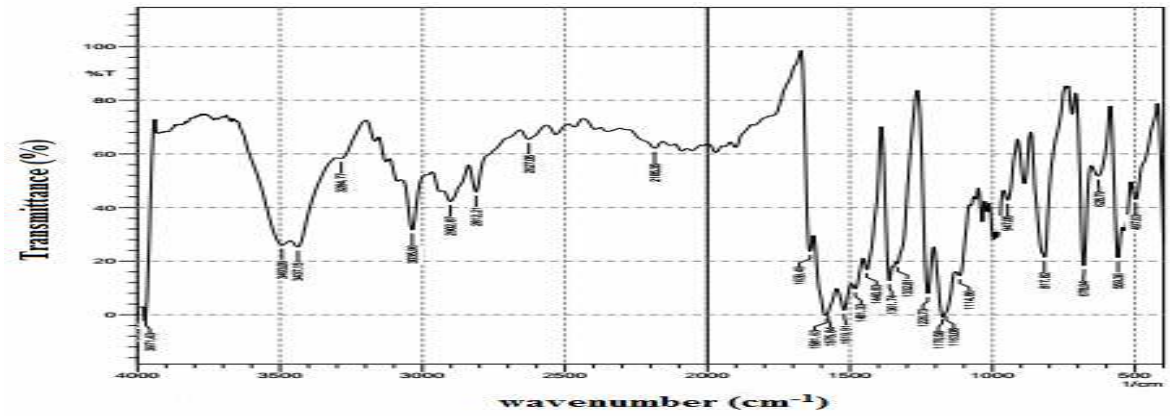

Fig.2. FT-IR spectrum of DAST

The optical absorption spectrum of DAST in methanol solution was recorded in the wavelength range 200-1100 nm using Varian Cary 5E UV - vis - NIR spectrophotometer. The UV cutoff wavelength of DAST occurs at 550 nm. It reveals that the grown crystal is transparent and useful for the second harmonic generation of Nd: YAG laser.

The thermal behavior of grown DAST crystal was investigated by Thermogravimetric and Differential Thermal Analysis (TG/DTA) which was carried out in nitrogen atmosphere at a heating rate of 10 °C/min. The decomposition of the sample starts around 300 °C.In the DTA trace, the presence of exothermic peak at 258.6°C corresponds to the melting point. It has been reported that DAST is known to thermally decompose above its melting temperature of 259 °C [4].

The Vickers hardness indentations were made on the as grown crystal of DAST on the (0 0 1) plane of the sample. The load was varied as 10, 20, 30, 40, 50, 60, 70 and 80 grams at room temperature. The corresponding diagonal length of the indentation mark was measured using Reichert MD 400E Ultra microhardness tester fitted with Vickers diamond indenter and attached to an incident light microscope. The indentation time was kept as 10s for all loads. The Fig.3 shows the variations of $H_v$with the applied load p. The hardness number for the sample is found to decreases with the applied load. Fig.4 shows the plot between log p

vs log d as a straight line. The slope gives the work hardening index 'n', which is found to be 3.97 for DAST crystal. The microhardness study indicates that the DAST belongs to the class of soft materials.

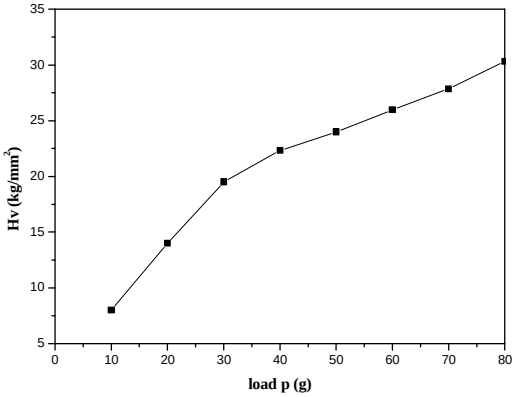

Fig.3. Variation of H_v with load for DAST crystal

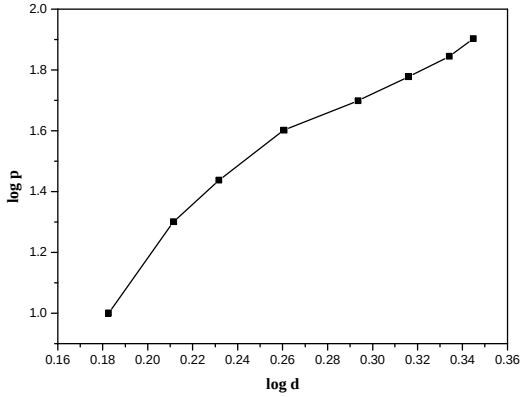

Fig.4. Plot between log p and log d for DAST crystal

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