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# Growth, spectral, optical and thermal studies of an organic single crystal 4-N, N'-dimethylamino-N-methylstilbazolium 4-aminotoluene-3-sulfonate

**Antony Raj[1], R. Gunaseelan[2], R. Jerald Vijay[3] and P. Sagayaraj[1]***

[1]Department of Physics, Loyola College (Autonomous), Chennai-600 034, India
[2]Department of Physics, Adhi College of Eng and Technology, Kancheepuram-631 605, India
[3]Department of Electrical Engineering, University of Chile, Santiago, Chile-8370451.

*Corres. author : psagayaraj@hotmail.com

**Abstract:** Terahertz (THz) applications based ionic organic nonlinear optical single crystals of 4-N, N'-dimethyl amino-N-methylstilbazolium 4-aminotoluene-3-sulfonate (DAAS) are synthesized and grown by slope nucleation method coupled with slow evaporation technique (SNM-SE). The single crystal X-ray crystallographic analysis revealed that the crystal structure of DAAS is triclinic with space group P1. The elemental composition, linear and nonlinear optical properties are observed by FT-IR, UV-Vis and Kurtz-Perry NLO test. The thermal stability of the DAAS crystal was investigated by TG/DTA analyses using Perkin Elmer TGA-7 spectrometer.
**Key words** - organic compound; crystal growth; nonlinear optical; thermal behavior.

## Introduction:

The syntheses of organic molecules with high nonlinearity have attracted much attention due to their potential applications in electro optic modulation, frequency conversion and terahertz wave generation [1]. Among the variety of organic materials, ionic organic crystals possess superior advantages compared non-ionic specious due to their high thermal, mechanical and photochemical stability combined with high chromophore concentration [2]. An ionic organic DAST (4-N, N-dimethylamino-N-methylstilbazolium tosylate) crystal is best example for this kind of materials with second harmonic generation SHG efficiency 1000 times than the reference urea at 1907 nm laser emission and also large second order NLO susceptibility $\chi^{(2)}$ = 2020±220 pm/V and electrooptic coefficient ($r_{11}$= 77 pm/V) at 800 nm making it a perfect choice for THz wave generation [3]. Recent studies are involved salt containing the chromophore of DAST combined with varietal counter ion afforded a number of new materials that are highly active for SHG [4-5]. It is proven that the stilbazolium cations are attractive species in ionic organic crystals because of the molecular nonlinearity can be simply preserved by varying the counter anions [6]. In this connection, Zun et al made an attempt to grow a

stilbazolium salt of 4-N, N dimethylamino-4' - N' -methyl stilbazolium 4-aminotoluene-3-sulfonate (DAAS) and has grown small size crystals [4]. The aim of the present study is to explore the synthesis, crystal growth, structural, spectroscopic, optical and thermal characterizations for better understanding of the tittle compound.

## Materials and method

DAAS was prepared by metathesization of the 4-N, N-dimethylamino-N'- methylstilbazolium iodide (DMSI) salt with sodium 4-aminotoluene-3-sulfonate. A green precipitate was obtained as a result of anion exchange reaction of DAAS. The purity of DAAS was further improved by successive recrystallization. Crystal growth was performed by employing slope nucleation coupled with slow evaporation technique (SNM-SE). For crystal growth, 1.0 g of DAAS was dissolved in 150 ml of methanol-water mixed solvents system (1:1) at 45 $^{o}$C. The solution was prepared in a Teflon beaker with a Teflon plate with parallel grooves which was sealed with a perforated lid. After 15-18 days of slow evaporations, crystals with size upto 2 x 0.5 x 0.5 mm$^3$ were harvested and they appeared typical red in colour (Fig. 1).

## Results and Discussion:

### Single crystal XRD analysis

The XRD data confirmed triclinic crystal structure of DAAS with noncentrosymmetric space group P1. The calculated lattice parameters are a (Å) = 7.2451, b (Å) = 8.953, c (Å) = 10.1010, α (deg) = 97.82, β (deg) = 110.41 and γ (deg) = 112.30. The data is almost in close agreement with the earlier report [4].

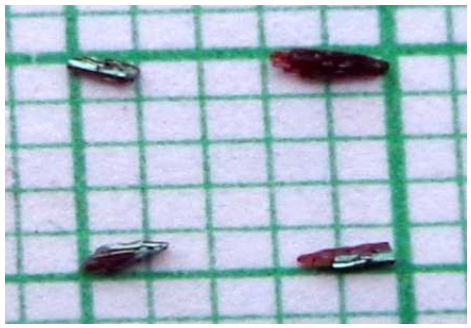

**Fig. 1** Photograph of DAAS crystals

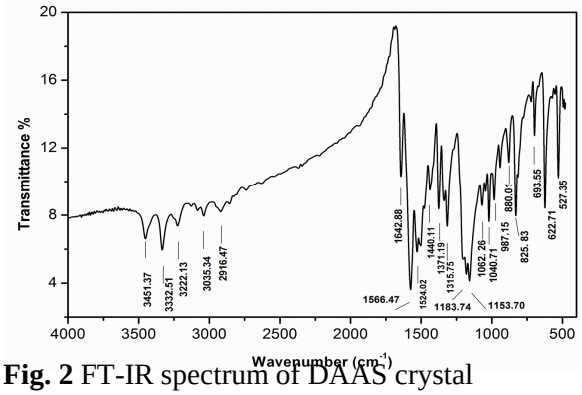


**Fig. 2** FT-IR spectrum of DAAS crystal

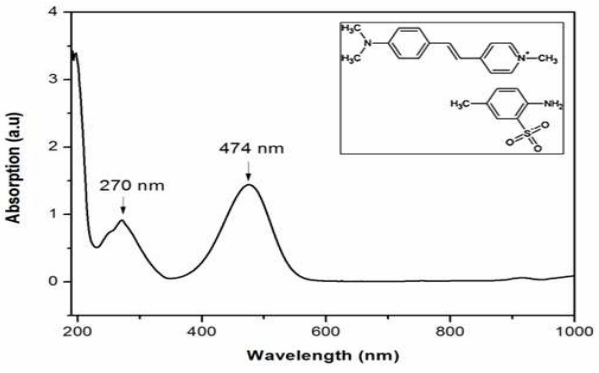


**Fig. 3** UV-Vis absorption spectrum of DAAS (inset) Molecular structure

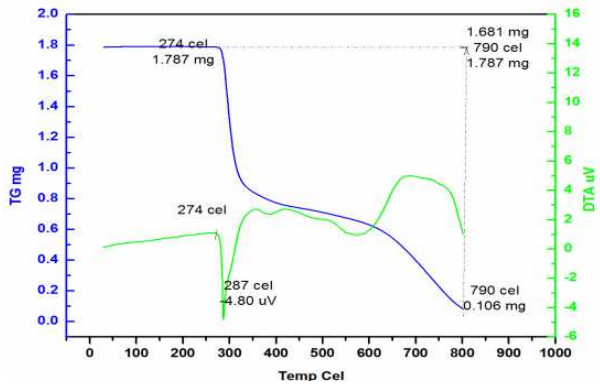


**Fig .4** TG/DTA curve of DAAS

### FT-IR analysis

The FTIR spectrum for DAAS crystal was recorded in the wavenumber range 400 to 4000 cm$^{-1}$. In Fig 2. The peak at 3451.37 and 3332.51 cm$^{-1}$ are assigned to N-H stretching of primary amine group present in the anion. The peak at 3035.34 cm$^{-1}$ is assigned to the aromatic C-H stretch. The peak seen at 2916.47 cm$^{-1}$ is assigned to the alkyl C-H stretch. The alkene bond stretching vibrations in conjugated systems without a centre of symmetry interact to produce two C=C stretching bands, near 1650 and 1600 cm$^{-1}$. The peak at 1371.19 cm$^{-1}$

corresponds to $CH_2$ bending and C-N stretching mode. The peak observed at 825.83 $cm^{-1}$ represents the 1, 4 distributed aromatic ring. The in-plane and out-plane deformations bands are observed, as expected, in the regions 1510-1000 $cm^{-1}$ and 1000-750 $cm^{-1}$, respectively. The spectrum further illustrates that the bands in the range 4000 to 2500 $cm^{-1}$ are relatively less intense, suggesting that the grown crystal is an ordered single crystal [5].

**UV-vis absorption study**

The absorption spectrum of DAAS was recorded in liquid phase using SHIMADZU 2450 spectrophotometer in the wavelength region 200–1000 nm. The absorption spectrum of DAAS (Fig.3) shows two distinct peaks at 270 nm and 474 nm. The minor peak at 270 nm corresponds to the n-π* transition and the major peak at 474 nm corresponds to π-π* transition. It has been reported that DAST and its derivatives are dissolved in methanol; it leads to dissociated state generating free cations and anions [5].

**Thermal analysis**

The TG/ DTA curves of DAAS sample were recorded between room temperature to 800 $^{o}$C in nitrogen atmosphere at a heating rate of 20 $^{o}$C/min. The TGA curve (Fig.4) illustrates a consecutive weight loss starting at 274 $^{o}$C. The DTA trace shows an endothermic peak at about 287 $^{o}$C which denotes the melting point of the material. Further, in DTA then material starts melting at exactly 274 $^{o}$C as we observed the weight loss in TGA. From this observation, it can be clearly stated that the crystal is thermally stable up to 274 $^{o}$C without any weight loss.

**Kurtz-Perry NLO test**

The SHG of DAAS was performed by Kurtz and Perry technique using Q-switched mode locked Nd: YAG laser operating at 1064 nm fundamental wavelength. For a laser input pulse of 6.2 mJ, the second harmonic signal of 1.4 V was produced in DAAS and the experimental data confirms that the SHG efficiency is nearly 31 times than that of standard urea (for Urea the output signal was 45 mV).

In summary, the growth of single crystal of DAAS is achieved. The structure and elemental composition are identified by single crystal XRD and FTIR. The UV-Vis spectrum showed a wide transparency between 550-1000 nm. The material showed high SHG efficiency compared to urea and posses good thermal stability. By carefully controlling the growth conditions, it is feasible to grow good quality single crystals of DAAS.

## References:

1. Ruiz B., Coe B.J., Gianotti R., Gramlich V., Jazbinsek M., and Gunter P., Polymorphism,,crystal growth and characterization of an organic nonlinear optical material: DAPSH, Cryst. Eng. Comm., 2007, 9, 772–776.
2. Jerald Vijay R., Melikechi N., Tina Thomas, Gunaseelan R., Antony Arockiaraj M. and Sagayaraj P., Investigation on the growth of DAST crystals of large surface area for THz applications, Mater. Chem. Phys., 2012, 132, 610-617.
3. Dai Y., Tan J., Ye N. and Yang Z., Synthesis and crystal growth of thienyl-substituted pyridinium derivatives for second-order nonlinear optics, Cryst. Eng. Comm., 2014,16, 636-641
4. Sun Z., Liu X, Wang X.Q., Li L., Shi X., Li S., Ji C., Luo J. and Hong M., Engineering of acentric stilbazolium salts with large second order optical nonlinearity and enhanced environmental stability M., Cryst. Growth Des., 2012, 12, 6181–6187.
5. Jerald Vijay R., Melikechi N., Tina Thomas., Gunaseelan R., Antony Arockiaraj M. and Sagayaraj P., Growth, structural, optical and thermal properties of potential THz material: N, N- dimethylamino-N′-methylstilbazolium 4-styrenesulphonate, J. Cryst. Growth, 2012, 338**,** 170–176.
6. Gu J, Chen W. Q., Wada T., Hashizume D. and Duan X.M., From supermolecular sheet to helix by breaking molecular symmetry: the case of 4-[2-(carbazol-3-yl) vinyl] pyridium tosylate, Cryst. Eng. Comm., 2007, 9, 541-544.

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