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Synthesis, growth and characterization of a novel organic nonlinear optical crystal 4-Chloro -N-methyl 4-stilbazolium tosylate

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ABSTRACT

A novel organic non-linear optical material 4-chloro -N- methyl 4-stilbazolium tosylate, a new derivative of the stilbazolium tosylate family has been synthesized and good optical quality single crystals of size 10 mm x 6 mm x 2 mm were grown by slow evaporation technique. The grown crystals were subjected to different instrumentation methods for characterization. The diffraction planes were identified and indexed by powder X-ray diffraction analysis. The crystal system and lattice parameters were found from single crystal X-ray diffraction. Fourier transform infrared was recorded to confirm the functional groups. In order to study the optical quality of the grown crystal, the UV-VIS spectrum was recorded in the solution state and cut off wavelength was determined. Vickers Microhardness test was carried out and Meyer's index 'n' was calculated. Being nonlinear optical material, second harmonic efficiency was determined in comparison with urea.

Keywords: Crystal Growth, Organic compounds, X-ray diffraction, Chemical synthesis, Optical properties

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INTRODUCTION

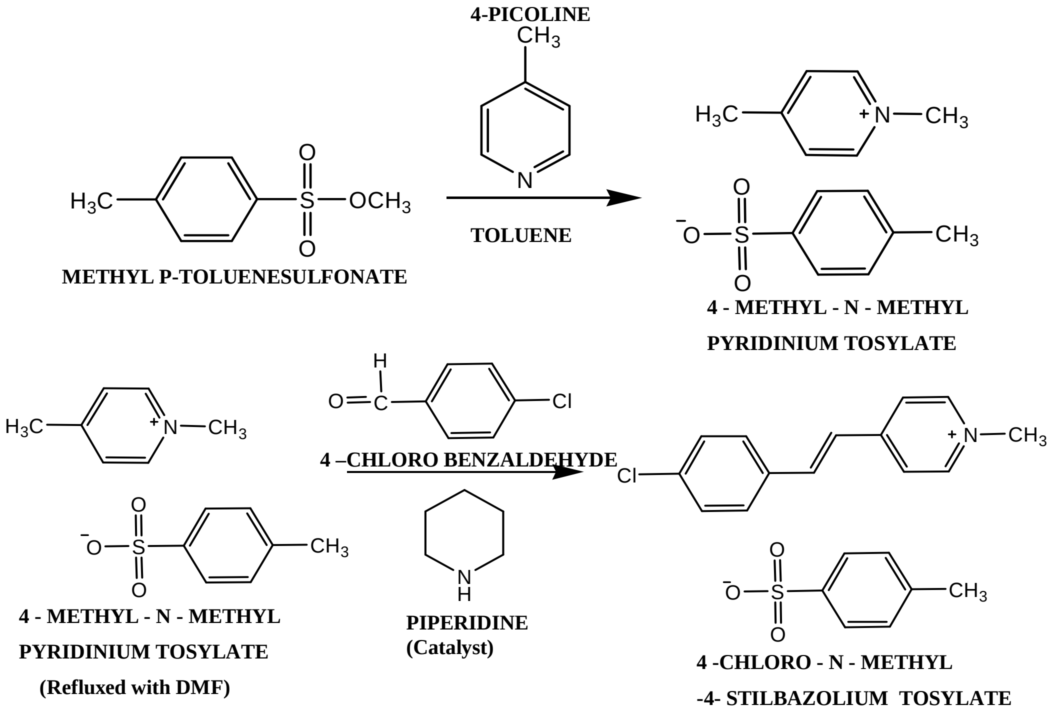
Organic nonlinear optical (NLO) materials have attracted much interest because of their large electro-optic coefficient, small dielectric constant, short-response time and large NLO properties. Well designed organic nonlinear optical materials are far superior to their inorganic counterparts, owing to their relatively high and much faster nonlinearities [1]. Among the various classes of materials investigated worldwide, ionic organic crystals are of special interest due to their advantageous mechanical, chemical and thermal properties. Among them, 4-dimethylamino-*N*-methyl-4-stilbazolium tosylate (DAST) is a promising material due to its much larger electro-optic coefficient ($r_{11} = 92 \pm 9$ pm/V at $\lambda = 720$ nm), NLO properties ($d_{11} = 1010 \pm 110$ pm/V at

λ = 1318 nm) and lower dielectric constant (ε = 5.2) [2]. Furthermore, DAST is a relatively hard material due to ionic bonds in its structure. Accordingly DAST crystals find application in the high-sensitive electric-field sensor and the source of THz wave with high-power and broadband [3]. Based on the excellent nonlinear optical properties of DAST, new organic nonlinear crystals based on strong Coulomb interactions to induce highly non-centrosymmetric and stable packing is being developed [1, 4]. Several research groups in the world are involved in the development of DAST [5-10] and its derivatives [11-15] for various applications using different crystal growth techniques. In this series, we have extended our effort in growing 4-chloro-N-methyl-4-stilbazolium tosylate (CMST) crystal and its various characterizations, which is a new derivative in the stilbazolium tosylate family with NLO property.

2. Synthesis and crystal growth

CMST was synthesized by the condensation of 4-methyl-N-methyl pyridinium tosylate, which was prepared from 4-picoline (C_6H_7N), methyl p-toluene sulfonate ($C_8H_{10}O_3S$) and 4-chloro-benzaldehyde (C_7H_5ClO) in the presence of piperidine as catalyst.

The step by step synthesis procedure of CMST is as follows: The calculated amounts of picoline (10.31 ml, 0.105 mol %) and methyl toluene sulfonate (15.88 ml, 0.105 mol %) were taken together with toluene solution (200 ml) in a round-bottomed flask (500 ml) of a Dean-Stark apparatus. Then the mixture was heated using a heating mantle until it was crystallized as a white salt, which was insoluble in toluene. While heating the mixture, dimethyl formamide solution was added to the toluene salt until the mixture salts are dissolved. After getting the clear solution of the above said mixture, the 4-chloro-benzaldehyde (14.76 g, 0.105 mol %) was added slowly.



Scheme 1. Synthesis of 4-chloro-N-methyl-4-stilbazolium tosylate

After the reaction process, the Piperidine was added as catalyst until the solution just turned to red colour. Then the mixture was refluxed with a Dean-Stark trap in order to remove water. After the collection of more than an equivalent amount of water the reactants were cooled to room temperature and the synthesized yellow colour CMST salt was collected. To prevent the absorption of water from the atmosphere, the collected material was kept in the oven at 100 °C for an hour. The synthesized material was dissolved in methanol, and was transferred to a glass tray with fine pored cover and was left undisturbed. Transparent crystals of size 10 mm x 9 mm x 2 mm (Fig. 1) were obtained after three successive recrystallization processes.

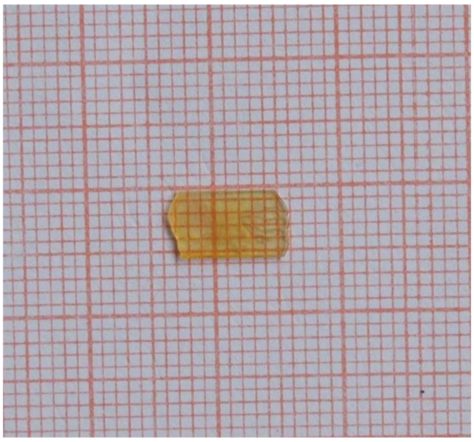


Fig. 1. Photograph of the as grown crystal

3. Characterization

The grown single crystals of CMST have been subjected to different instrumentation methods such as powder X-ray diffraction, Single crystal X-ray diffraction, Fourier Transform Infrared (FTIR) and UV- transmission Spectroscopic Studies and Powder SHG measurements.

3.1. Single crystal X-ray diffraction

Single crystal X-ray diffraction analysis was performed by means of Bruker Smart Apex Instrument with Mo Kα radiation of wavelength 0.7170 Å. The calculated lattice parameters shows that it belongs to monoclinic system with the parameters a = 9.041(3) Å, b = 6.437(2) Å, c = 33.788(5) Å, β = 94.31(3) ° and Volume = 1960.9 $Å^3$

3.2. Powder X-ray diffraction

Powder X-ray diffraction study was carried out using Rich Seifert X-ray diffractometer with the CuKα radiation (λ = 1.5418 Å) in the range of 10 ° - 35 °, in steps of 0.02 °. It reflects good crystallinity of the grown crystal. The lattice parameters were calculated using TREOR program which coincide with the single crystal XRD results and the peaks were indexed using APPLEMAN program from the observed 2 θ values. The recorded spectrum is shown in Fig. 2.

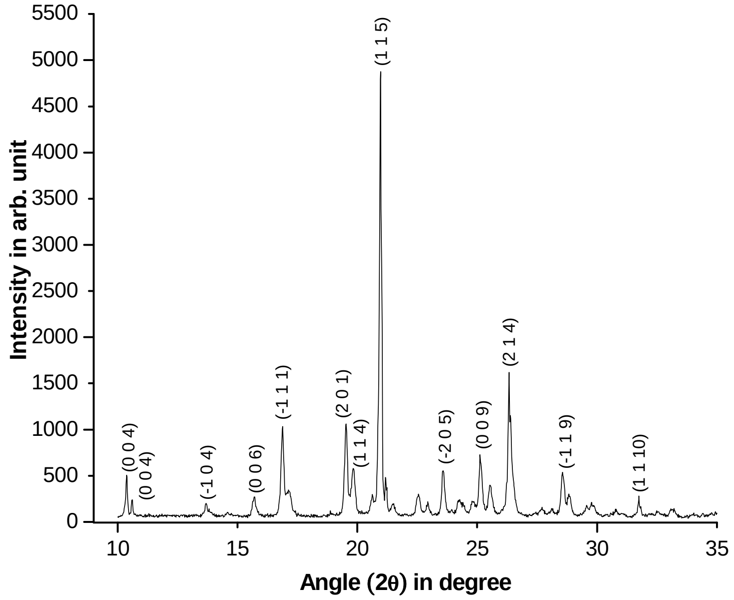


Fig. 2 Powder XRD pattern of CMST

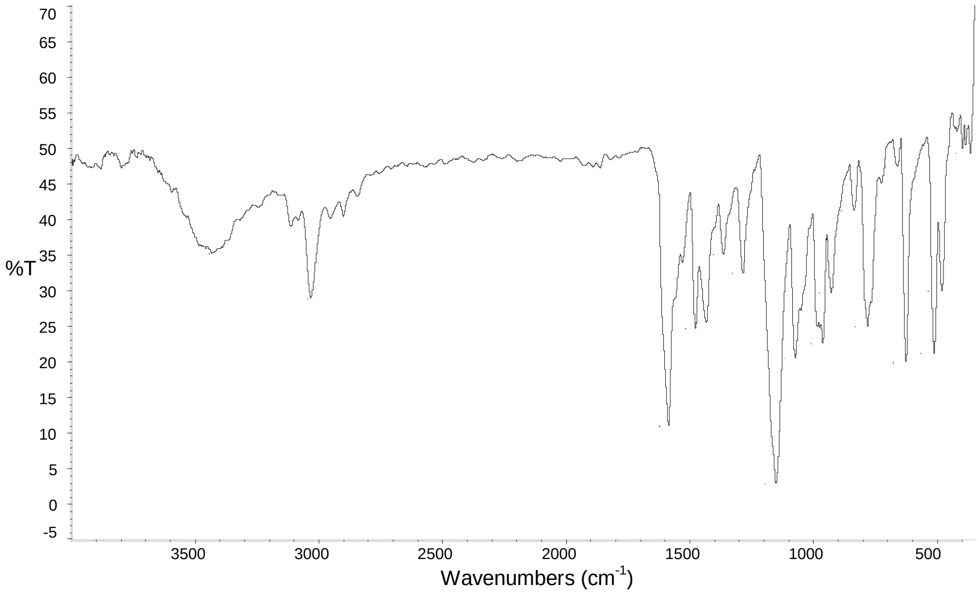


Fig. 3. FTIR spectrum of powdered CMST crystal

3.3. Fourier transform infrared spectroscopic studies

The Fourier transform infrared spectral analysis is a technique in which almost all functional groups in a molecule absorb characteristic frequencies. The Fourier transform infrared spectrum was recorded for the powdered sample with AVATAR330 FTIR spectrometer in the region 4000--400 cm^{-1} using the KBr pellet technique. Figure 3 shows the FTIR spectra of the CMST sample and the functional groups are analyzed taking into account the molecular structure of the material. The peak at 3047 cm^{-1} corresponds to aromatic C-H stretching vibration. The narrow peak observed at 1622 cm^{-1} belongs to C-C stretching of the olefinic double bond. The peaks at 1516 and 1471 cm^{-1} are assigned to aromatic ring skeletal in plane stretching vibration. Asymmetric and symmetric stretching vibrations of sulphonate group ascertained to peaks at 1327 and 1196 cm^{-1}. The peaks at 1009 and 831 cm^{-1} are due to Phenolic C-O stretching vibration and Olefinic C-H bond respectively, and the peak at 677 cm^{-1} refers to the Cis orientation of the substitute at the olefinic double bond.

3.4. UV- transmission spectrum

The transmission spectrum of CMST was recorded using HITACHI model U2800 double beam spectrophotometer in the wavelength range 1100 nm – 200 nm by dissolving the powdered sample in methanol (Fig. 4) and cut off wavelength is found at 387 nm. Absence of absorption in the region between 400 and 1100 nm is an advantage as it is the key requirement for materials having NLO properties [16].

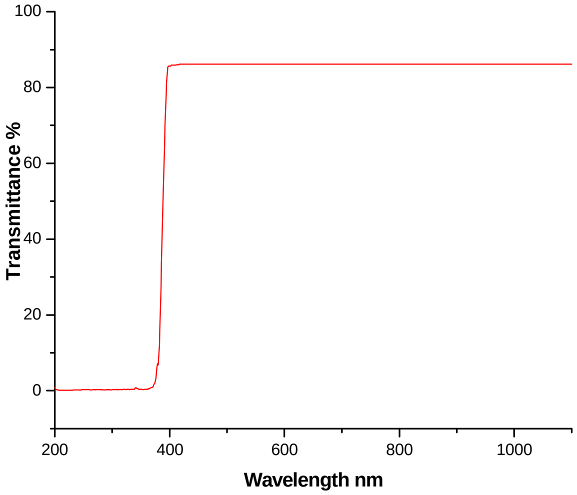


Fig. 4. UV – transmission spectrum of CMST in solution form

3.5. Vickers microhardness studies

The mechanical strength of the crystal was studied using an MH-112 Vickers microhardness tester (Japan). Vickers hardness indentations were made on the flat polished face of the crystal at room temperature for loads 10, 25, 50 and 100 g using Vickers hardness tester fitted with Vickers diamond intender and attached to an incident light microscope. Crack initiation and material chipping became significant beyond 100 g of the applied load and hardness test thus could not be carried out further. The lengths of the two diagonals of the indentations were measured and the Vickers hardness number was computed using the formula $H_v = 1.8544\ P/d^2$, where H_v is the Vickers hardness number in kg mm^{-2}, P is the intender load in kg and d is the diagonal length of the impression in mm. The variation of H_v with load and plot of log P vs. log d are shown in Fig. 5 and 6. It is evident from the fig.5 that H_v increases with increase in P due to reverse size indentation effect [17]. The Meyers index number '*n*' is estimated as 3.588 from the slope of the graph 6. From the Meyer's index number it is clear that it belongs to soft material category [18, 19].

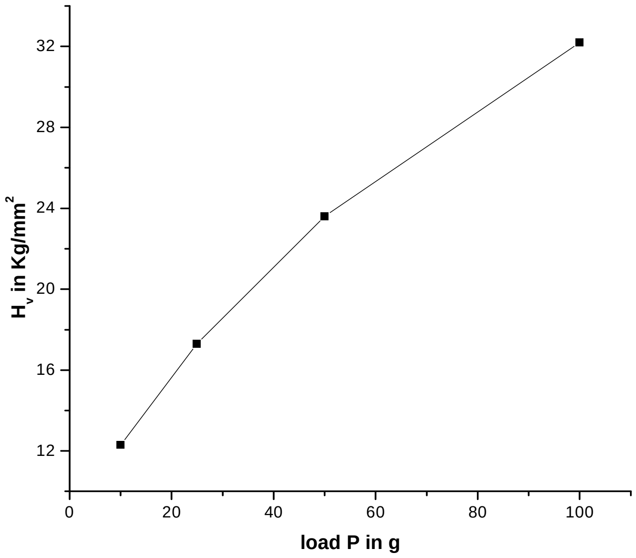


Fig. 5. Variation of hardness number *Hv* with Load

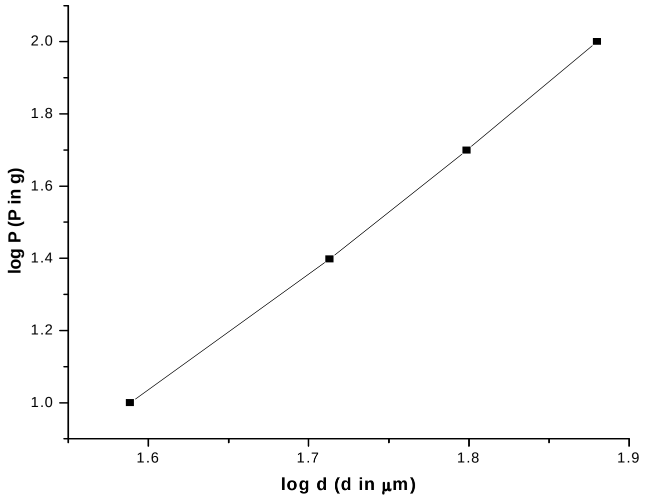


Fig. 6. Graph showing log *d* Vs log *P*, the slope of this line gives the Meyers index number

3.6. Powder SHG test

A preliminary study on the second harmonic generation efficiency of the crystal with reference to urea was carried out by Kurtz powder technique developed by Kurtz and Perry [20]. The crystal was ground to homogeneous powder and tightly packed in a micro capillary tube and mounted in the path of the Q-switched Nd:YAG laser beam emitting 1064 nm, 10 ns pulse width and 5 mJ power. The generated SHG signal at 532 nm is split from the fundamental frequency using an IR separator. A detector connected to power meter is used to detect second harmonic intensity and read the energy input and output. The SHG efficiency is compared with urea. From SHG test, the SHG efficiency of the grown CMST crystal was found to be nearly 10.2 times greater than that of urea.

CONCLUSION

The title compound CMST was successfully grown by slow evaporation technique. From the powder X-ray diffraction and single crystal X-ray diffraction pattern, the lattice parameters were calculated, and the monoclinic structure is confirmed. The functional groups were identified from the FTIR spectrum. SHG efficiency of CMST was found to be 10.2 times greater than that of urea. From the microhardness measurements, it was observed that the hardness increases with the increase of load. Meyer's index measurement shows that the crystal belongs to soft material category.

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