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Research Paper

Surface Analysis of 4-Chloro N-Methyl 4-Stilbazolium Tosylate Single Crystal

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A new organic material 4-chloro N-methyl 4-stilbazolium tosylate, a derivative of the stilbazolium family, known for efficient nonlinear optical materials, has been synthesized for the first time. Employing slow evaporation technique transparent optically good quality single crystals of size 9 mm x 5 mm x 2 mm were grown from methanol. The cell dimensions obtained by single crystal X-ray diffraction studies reveal that the crystal belongs to the monoclinic system. Microhardness studies revealed that the hardness of the grown crystal increases with an increase in load. Meyer's index number *n* was calculated and it was found that the material belongs to soft material category. Etching studies were made on the crystal surface.

Key Words: Microhardness; Anisotropy; Etching; Laser Damage Threshold

1. 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 ± 9 pm/V at λ = 720 nm), NLO properties (d_{11} = 1010 ± 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. Experimental Methods

2.1 Sample Preparation

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

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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. 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 9 mm x 5 mm x 2 mm (Fig. 1) were obtained after three successive recrystallization processes. Crystals with flat and smooth faces, free from any damages were selected for static indentation studies. The (010) surface of the selected crystal was polished gently with methanol before carrying out the measurements.

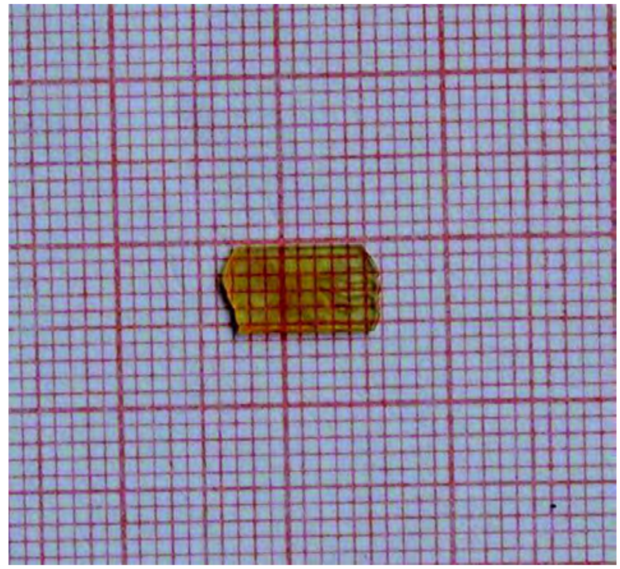

Fig. 1: Grown crystal of CMST

2.2 Microhardness Measurements

Indentations were made on a selected crystal, using Mitutoyo MH-112 Microhardness tester (Japan). The crystal was mounted properly on the base of the microscope and the selected face was indented gently by varying the loads from 10 to 50 g for a dwell period of 10 s using both Vickers diamond pyramid indenter and Knoop indenter attached to an incident ray research microscope. The Vickers indented impressions were approximately square in shape. The length of the two diagonals was measured by a calibrated micrometer attached to the eyepiece of the microscope after unloading. For a particular load, at least five well-defined impressions were considered and the average of all the diagonals (*d*) was considered. The Vickers hardness number (H_v) was calculated using the standard formula,

$$H_v = 1.8544 \, P / d^2 \quad (1)$$

where *P* is the applied load in kg, *d* in mm and H_v in kgmm^{-2}.

The Knoop indented impressions were approximately rhombohedral in shape. The long diagonal length (*d*) was considered for the calculation of the Knoop hardness number (H_k) using the relation,

$$H_k = 14.229 \, P/d^2 \quad (2)$$

where *P* is the applied load in kg, *d* in mm and H_k in kgmm^{-2}.

Crack initiation and material chipping become significant beyond 50 g of the applied load. So hardness test could not be carried out above this load. The elastic stiffness constant (C_{11}) is calculated (Table 1) using Wooster's empirical relation [16],

$$C_{11} = H_v^{7/4} \quad (3)$$

As indentation initiates plastic deformation in a crystal, which is highly directional in nature, the hardness measurement may be a function of the orientation of the indented crystal. Thus, any anisotropic effect shown by the size of the indentation mark is reflected in hardness number. To study the hardness anisotropy present in CMST crystal, the crystal was mounted on the stage of the microscope properly and indented. The initial position (0º) of the index line was set, with one of the diagonals of the indented impression and the stage of the microscope was then rotated keeping the indenter fixed and H_v was measured at every 30º interval.

2.3 Etching Studies

The etching studies were carried out in order to know the quality of the grown crystal. Methanol, ethanol, and acetone were used as etchants. All surfaces of the specimen were etched for 15 s and the patterns were examined by an optical microscope before and after the application of the etchant.

3. Results and Discussion

3.1 Vickers Hardness Test

The dependence of Vickers microhardness on load shows different behavior for different types of materials. The dependence of H_v with load may be summarized as following four types

(i) H_v may remain constant irrespective of the amount of applied load [17] as suggested by Meyer's law [18],

$$P = kd^n \tag{4}$$

where $n = 2$ (Meyer's index number) accounts for this type of behavior.

(ii) H_v increases with increasing load. According to Onitsch this type of behaviour is applicable to materials with Meyer's index $n > 2$ [19-21].

(iii) H_v decreases with increasing load, for materials with $n < 2$ [22, 23].

(iv) H_v shows complex variation with applied load [24].

Fig. 2 shows the variation of H_v as a function of applied load ranging from 10 g to 100 g on (010) face

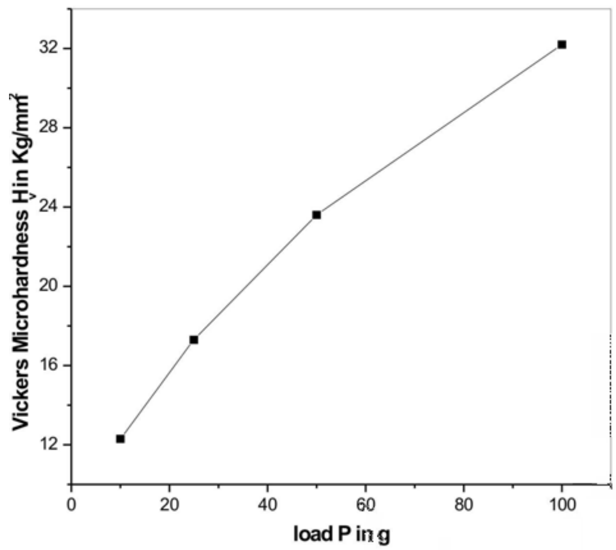

Fig. 2: Variation of H_v with load

for CMST crystal. It is very clear from the figure that H_v increases with increase of load. It was not possible to go beyond a load of 100 g as the material then got damaged around indentation.

The Meyer's index number was calculated from the Meyer's law, which relates the load and indentation diagonal length (4).

$$\log P = \log k + n \log d \tag{5}$$

where k is the material constant and n is the Meyer's index. Plot of log P *versus* log d gives a straight line (Fig. 3) and slope of the line yields the value of 'n'. The calculated value of 'n' is 3.426, from the expression $H_v = bP^{(n-2)/n}$, H_v should increase with increase of P if $n > 2$ and decrease with same if $n < 2$. The 'n' value agrees well with the experiment.

As observed in the literature, for most of the materials, H_v initially decreases with load and then attains saturation based on the phenomenon of indentation size effect (ISE) which usually involves a decrease in microhardness with increasing applied test load [25]. In our case, the microhardness increases with load based on the phenomenon of reverse ISE. This has been explained in terms of the existence of a distorted zone near the crystal medium interface, and effects of vibration. According to Onitsch [21] 'n' should lie between 1 to 1.6 for harder materials and above 1.6 for softer materials. Thus CMST belongs to soft material category.

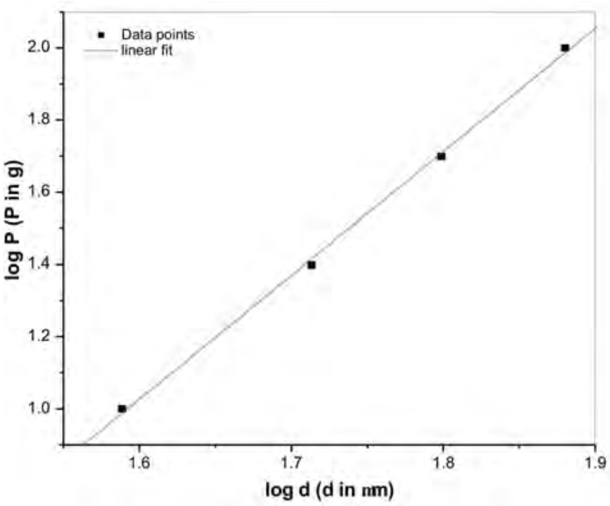

Fig. 3: Graph between log P Vs log d

Strength of a material is its ability to resist deformation under the action of applied load. For a particular value of the load the material ceases to resist and yields. At this point large deformation takes place without any increase in load. The value of hardness of the material corresponding to this point is called yield strength (σ_y). It is calculated using the microhardness H_v and Meyer's index *n*. For materials having $n > 2$,

$$\sigma_y = (H_v/2.9)[1-\{n-2\}]\ [12.5\ (n-2)/1-(n-2)]^{(n-2)} \quad (6)$$

and

$$\sigma_y = H_v/3, \text{ when } n < 2 \quad (7)$$

Since Meyer's index *n* is greater than 2 for the title crystal, eqn. (7) is used to calculate the yield strength and it varies from 2.993 to 4.776 for the application of load from 10 to 100 g. The resistance pressure is defined as; a minimum level of indentation load (W) below which there is no plastic deformation [26]. Hays and Kendall proposed a relationship to calculate the 'W' by the equation

$$d^n = W/k_1 + (k_2 / k_1)\, d^2 \quad (8)$$

The plot between d^n and d^2 gives a straight line (Fig. 4) having slope k_2/k_1 and intercepts W/k_1. Knowing the value of n as 3.426, the value of W was calculated to be 9.793 g.

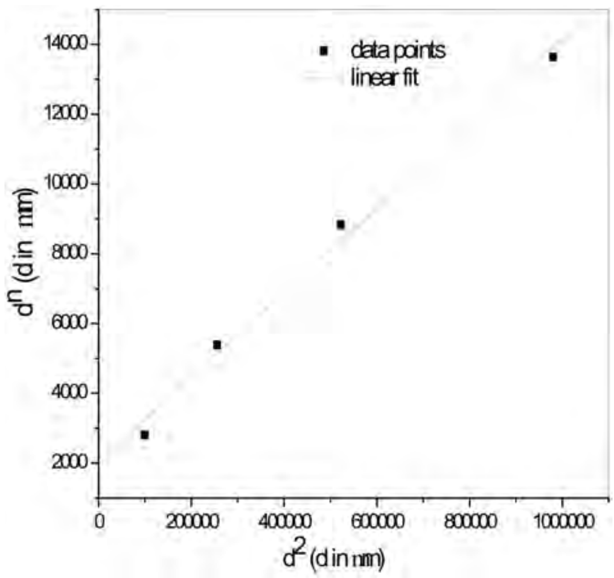

Fig. 4: Graph between d^n and d^2

The elastic stiffness constant (c_{11}) was calculated by Wooster's empirical relation. The calculated stiffness constant for different loads are tabulated.

Table 1: Load *versus* stiffness constant

S.No.	Load (g)	c_{11} (Pa)
1	10	80.786
2	25	146.751
3	50	252.695
4	100	435.259

Resistance to fracture indicates the toughness of a material. The fracture toughness K_c determines how much fracture stress was applied under uniform loading. It is an important parameter for the selection of materials for application where the load exceeds the limit or yield point. The crack developed on a crystal determines the fracture toughness K_c. If P is the applied load in Newton, c is the crack length measured from the center of indentation mark to the crack end in micrometer and *a* the half length of the square indentation, K_c can be calculated using the relation, [26]

$$K_c = P/\beta_0\, al^{1/2} \quad (9)$$

where l = c–a is the mean crack length, β_0 is a constant that depends upon the indentation geometry and for Vickers indenter β_0 is equal to 7. This equation gives a satisfactory value of the fracture toughness only when c/a < 2.5 (where a = d/2), that is, for Palmqvist cracks. For CMST crystal the value of c/a was 2.214 and the calculated K_c was 12.647 kg.m$^{3/2}$. The brittleness is an important property of the crystal which determines the fracture without any appreciable deformation. It is expressed in Brittle index B_i and is computed using the formula [26]

$$\text{Brittle index } B_i = H_v / K_c \quad (10)$$

The calculated value of B_i was 3.463 m$^{-1/2}$.

For studying the crystal anisotropy, the microhardness was measured by varying the crystal orientation over the range of 0º-360º in steps of 30º. No distortion in shape of the indentation was observed with the crystal orientation. From figure 5, it is clear that the variation was periodic, the maximum hardness number ($H_v$max) was observed at equal intervals (30º, 90º, 150º, 210º, 270º, 330º).

The variation in hardness number indicates the anisotropic nature of CMST crystal. The crystal structure and the slip system play an important role in the observed variation of hardness with crystal orientation. The directional variation in hardness might be due to the change in orientation of the slip system of the crystal with respect to the indenter.

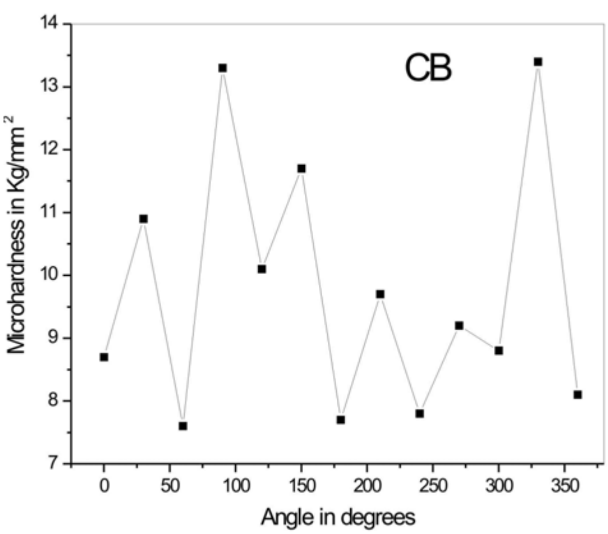

Fig. 5: Anisotropy nature of CMST crystal

3.2 Knoop Microhardness

The graph was plotted against Knoop hardness (H_k) and Load (P). The plot is shown in Fig. 6. From this measurement, it was found that as the load increases, the Knoop micro hardness number also increases. From the Knoop microhardness measurements the Young's modulus (E) of the crystal was calculated using the relation [27]

$$E = 0.45H_k/(0.1406 - b/a) \quad (11)$$

where H_k is the knoop microhardness value at a particular load, b and a are the shorter Knoop indentation diagonal and the longer indentation diagonal respectively. The calculated Young's Modulus is 1.1064 x 10^{10} Nm^{-2}.

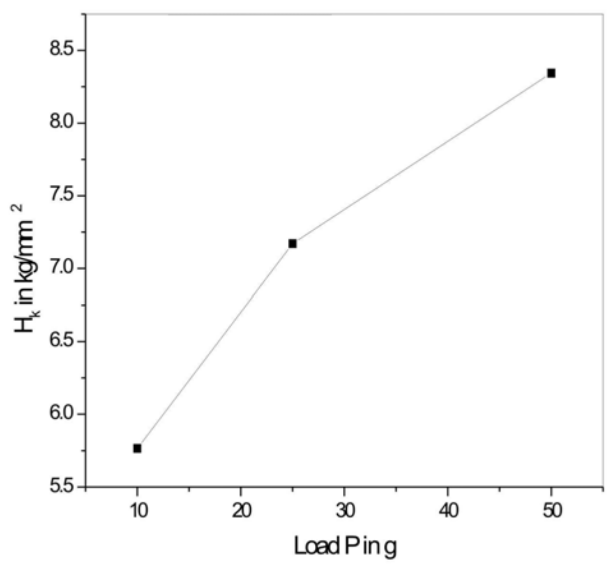

Fig. 6: Variation of Knoop hardness H_k with load

3.3 Etching Studies

Dislocations influence a number of physical properties like plasticity and mechanical strength. Hence it is necessary to study the dislocation [28]. The crystal surfaces were polished before the etching study using soft velvet cloth, and then the polishing suspension of colloidal silica with a grain size of 0.04 mm was utilized for final touches. All surfaces were etched in ethanol for 15 s and the etched patterns were examined by an optical microscope. Fig. 7 shows the optical microscope images of the CMST crystal surface after

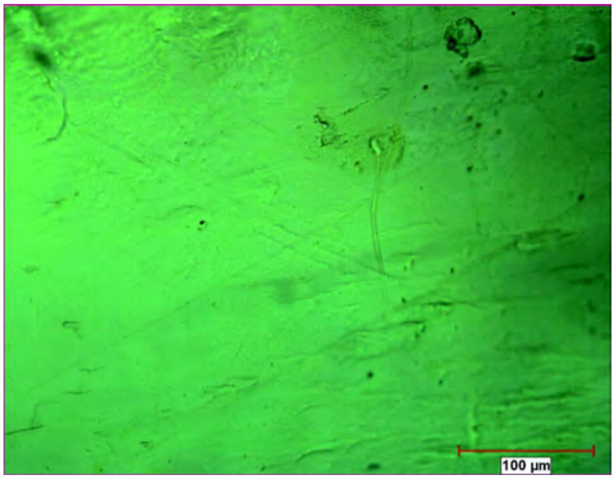

Fig. 7: Optical micrograph of etched surface of the crystal

the etching process. Tiny etch pits were formed on the surface of the grown crystal. The density of etch pits is quite high but their size is very small. From the study of the etch pattern, it is clear that there has been a selective etching at some specific sites [29].

3.4 Laser Damage Threshold

For nonlinear optical applications, one of the most important considerations in the choice of materials is its tolerance. This is the main criterion that restricts the application of many materials. Since high optical intensities are involved in nonlinear processes, NLO materials must be able to withstand high power intensities [30]. The energy density of the material was calculated using the formula, energy density = E/A, where E is the input energy measured in mJ and A is the area of the circular spot. The laser damage threshold was found to be 0.8912 GW/cm^2, which is higher than potassium dihydrogen phosphate (0.2) and lesser than urea (1.5) crystals [31].

Fig. 8: Optical micrograph of the CMST crystal surface after passing laser beam of 16.7 mJ for 30 s time

4. Conclusion

1) The Vickers Microhardness number, H_v for 4-chloro N–methyl 4-stilbazolium tosylate (CMST) single crystal, was calculated by the application of load in the range 10-50 g.

2) The H_v increases with increasing load. This type of variation in H_v can be explained by reverse indentation size effect, and confirmed by Meyer's relation.

3) The value of Meyer's index was calculated as 3.426, which suggests that the CMST belongs to soft material category.

4) The hardness versus load characteristic curve of CMST is in good agreement with the Heys and Kendall's theory of resistance pressure. The minimum load needed to initiate the plastic deformations in the surface was calculated.

5) The value of c_{11} gives an idea of toughness of bonding between neighboring atoms. Here, CMST has small value of c_{11}, which indicates

that the binding forces between the ions are not too strong.

6) The Knoop Microhardness test was also carried out by applying the load of range 10-50 g. It is observed that the H_k increases with increasing load.

7) The Young's modulus is calculated from the diagonal lengths of Knoop indentation.

8) The crystal has very good laser damage threshold value of 0.8912 GW/cm^2. Very minimum amount of defects were found from etching analysis.

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