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# MICROHARDNESS STUDIES AND SURFACE ANALYSIS OF 4-HYDROXY N-METHYL 4-STILBAZOLIUM BESYLATE SINGLE CRYSTAL

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## ABSTRACT

The Vickers and Knoop Microhardness studies were carried out on 4 - hydroxy N–methyl 4-stilbazolium besylate single crystal, subjected to loads 10, 25 and 50 g. The measurements were made at room temperature with the indentation time as 10 s. The Vickers hardness number and the Knoop Microhardness number were found to increase with the applied load due to reverse indentation size effect. The Meyer's index number, fracture toughness, brittle index and yield strength were calculated from Vickers hardness value. The Young's modulus was calculated using the Knoop hardness value. Hardness anisotropy has been observed in accordance with the orientation of the crystal. Laser damage threshold studies have been carried out for the crystal using a Q-switched Nd:YAG laser of 10 ns pulses. The surface of the grown crystal was analysed with etching. The results are discussed in detail.

**Key words:** *Microhardnes, Etching and Anisotropy.*

## 1. Introduction

Hardness is an important solid state property commonly used to determine the mechanical characteristics of the crystals. Hardness measurement is very important for device fabrications. Unlike other tests, hardness studies do not require large specimen, it is non-destructive and will quickly yield quantitative information about the mechanical strength of the materials. Microhardness testing is one of the best methods for understanding the mechanical properties of materials such as elastic constants, yield strength, plasticity, hardness anisotropy, creep behaviour and fracture behaviour [1]. The microhardness is a mechanical parameter which is strongly related to the structure and composition of the crystalline solids. It is the measure of the resistance that a crystal lattice offers to the motion of dislocations [2].

Many researchers have investigated the mechanical properties of different crystals. Vickers microhardness studies on solution grown single crystals of L-asparagine have been reported by Mohd Shakir et al [3], alkaline earth nitrates by Raja Shekar et al [2], lead titanate ceramics by Ravender Tickoo et al [4], flux grown holmium orthoferrite single crystals by Monita Bhat et al [5] and 4-N, N-dimethylamino 4'-methyl stilbazolium tosylate by Haja Hameed et al [6]. In the recent period we have undertaken considerable amount of work on microhardness studies on a number of crystals like cadmium mercury thiocyanate [7], stilbazolium tosylate derivatives [8], urea L-alanine acetate [9] and brushite [10]. The present investigation covers the Vickers and Knoop microhardness measurement of 4- hydroxy N–methyl 4-stilbazolium besylate single crystal, a new organic nonlinear optical material reported in the stilbazolium family [11].

## 2. Experimental Methods

### 2.1 Sample preparation

` Single crystals of 4- hydroxy N–methyl 4-stilbazolium besylate (HMSB) used for present investigation were grown from methanol by slow evaporation of the solvent at room temperature. After a growth period of 35 days, optically transparent crystals were harvested. Crystals with flat and smooth faces, free from any damage having an approximate dimension of 3 x 3 x 2 $mm^3$ were selected for static indentation studies. The (010) surface of the selected crystal was polished gently with methanol before carrying out the measurements.

### 2.2 Micro hardness measurements

The Vickers indented impressions were approximately square in shape. The length of the two diagonals was measured by a calibrated micrometer

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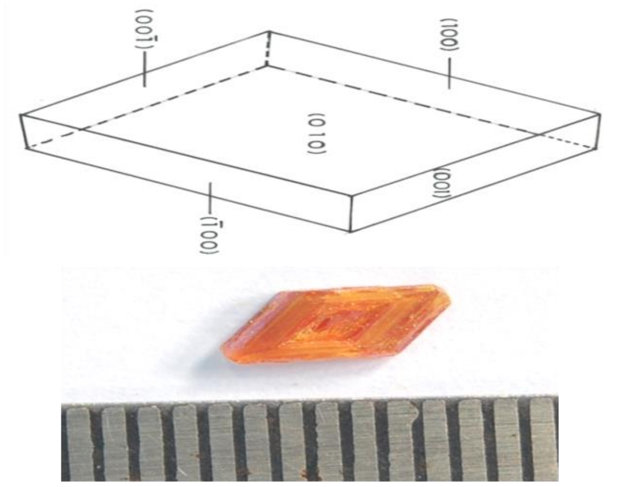

**Fig. 1: Photograph of the Grown HMSB Crystal And its Morphology Diagram**

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,

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

where P is the applied load in kg, d in mm and $H_v$ in $kg/mm^2$.

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,

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

where P is the applied load in kg, d in mm and $H_k$ in $kg/mm^2$.

Crack initiation and materials 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 using Wooster's empirical relation [12],

$C_{11}=H_v^{7/4}$ (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 HMSB 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 behaviour for different types of materials. The dependence of Hv with load may be summarized as following four types

(i) Hv may remain constant irrespective of the amount of applied load [13] as suggested by Meyer's law [14],

$P = kd^n$ (4)

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

(ii) $H_v$ increases with increasing load. According to Onitsch this type of behaviour is applicable to materials with Meyer's index $n > 2$ [7, 15-17].

(iii) $H_v$ decreases with increasing load, for materials with $n < 2$ [6, 8, 18, 19].

(iv) $H_v$ shows complex variation with applied load [3, 20].

Fig. 2 shows the variation of $H_v$ as a function of applied load ranging from 10 g to 50 g on (010) face for HMSB crystal. It is very clear from the figure that Hv increases with increase of load. It was not possible to go beyond a load of 50 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).

$\log P = \log k + n \log d$ (5)

where k is the material constant and n is the Meyer's index.

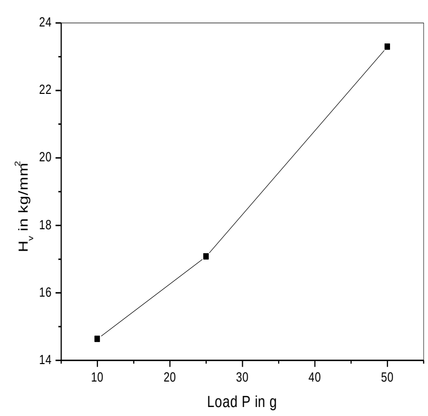


**Fig. 2 Variation of $H_v$ with load**

 

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 2.756, 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, Hv 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 [21]. 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 [17] 'n' should lie between 1 to 1.6 for harder materials and above 1.6 for softer materials. Thus HMSB belongs to soft material category.

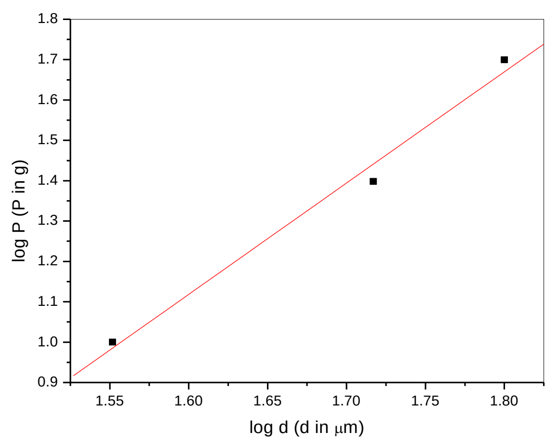


**Fig. 3 Graph between Log p versus Log d**

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 ($\sigma_y$). It is calculated using the microhardness Hv and Meyer's index n. For materials having $n > 2$,

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

and $\sigma_y = Hv/3$, when $n < 2$. (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 50 g. The resistance pressure is defined as; a minimum level of indentation load (W) below which there is no plastic deformation [22]. 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 2.756, the value of W was calculated to be 4.877 g.

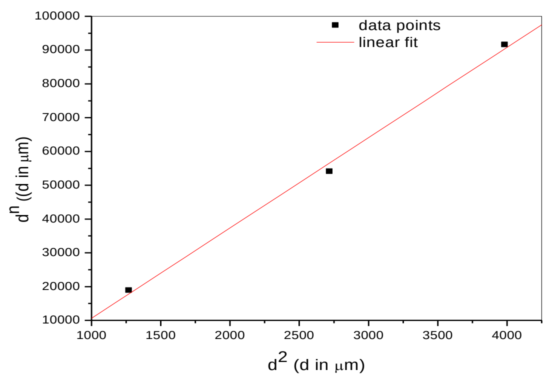


**Fig. 4 Graph between $d^n$ and $d^2$**

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

**Table 1: Stiffness Constant for Different Loads**

| S. No | Load (g) | $c_{11}$ x $10^{14}$ (Pa) |
|---|---|---|
| 1 | 10 | 1.09047948 |
| 2 | 25 | 1.43794804 |
| 3 | 50 | 2.47100066 |

Resistance to fracture indicates the toughness of a material. The fracture toughness Kc 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 Kc. 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, Kc can be calculated using the relation, [22]

$$K_c = P / \beta 0 \, a l^{1/2} \quad (9)$$

where $l = c – a$ is the mean crack length, β0 is a constant that depends upon the indentation geometry and for Vickers indenter β0 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 HMSB 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 Bi and is computed using the formula [22]

Brittle index $B_i=H_v/K_c$ (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 insteps 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, 120º, 180º, 240º, 330º).

The variation in hardness number indicates the anisotropic nature of HMSB 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.

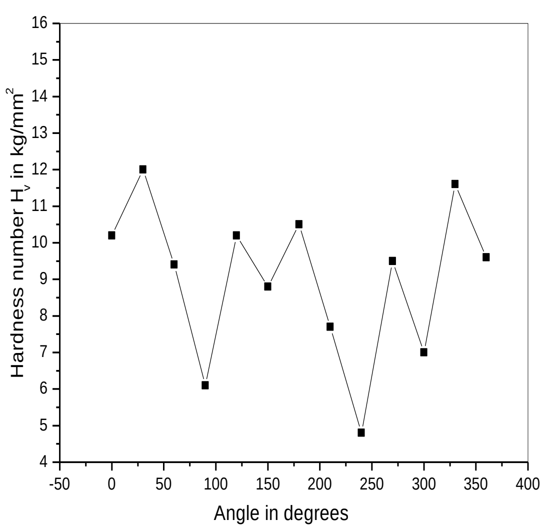


**Fig. 5 Anisotropy Nature Of Hmsb Crystal**

## 3.2 Knoop microhardness

The graph was plotted against Knoop hardness ($H_k$) and Load (P). The plot is shown in Figure 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 [23]

E = 0.45Hk/(0.1406 – b/a). (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 1010 N $m^{-2}$.

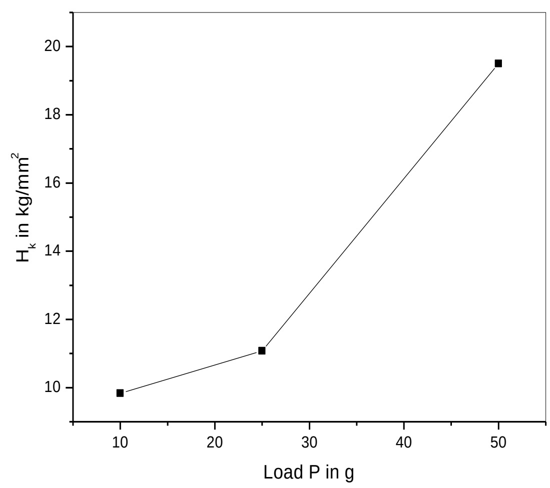


**Fig. 6 Variation of Knoop Hardness $H_k$ With Load**

## 3.3 Etching studies

Dislocations influence a number of physical properties like plasticity and mechanical strength. Hence it is necessary to study the dislocation [24]. 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 HMSB crystal surface after the etching process. Tiny etch pits were formed on the surface which also reveals the surface structure 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 [25].

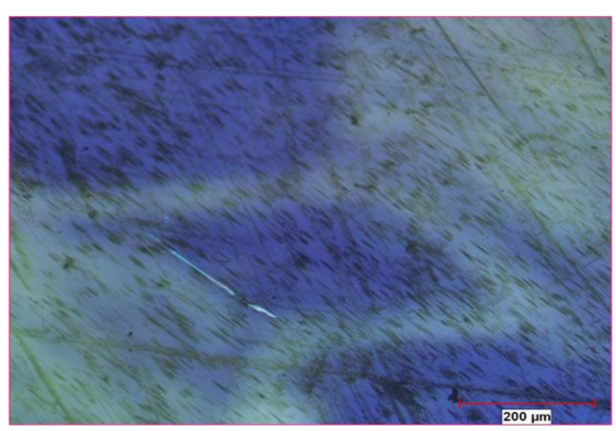


**Fig. 7 Optical Micrograph of Etched Surface of Crystal.**

### 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 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 [27].

## 4. Conclusion

i. The Vickers Microhardness number, Hv for 4 - hydroxy N–methyl 4- stilbazolium besylate (HMSB) single crystal, was calculated by the application of load in the range 10 – 50g.
ii. The Hv increases with increasing load. This type of variation in Hv can be explained by reverse indentation size effect, and confirmed by Meyer’s relation.
iii. The value of Meyer’s index was calculated as 2.756, which suggests that the HMSB belongs to soft material category.
iv. The hardness versus load characteristic curve of HMSB 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.
v. The value of $c_{11}$ gives an idea of toughness of bonding between neighboring atoms. Here, HMSB has small value of $c_{11}$, which indicates that the binding forces between the ions are not too strong.
vi. 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.
vii. The Young’s modulus is calculated from the diagonal lengths of Knoop indentation.
viii. 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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