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Mechanical properties of meta-nitroaniline NLO single crystals

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Vickers and Knoop microhardness studies were carried out on meta-Nitroaniline crystals grown by a slow evaporation technique over a load range of 10–100 g. The Vickers and knoop microhardness numbers (H_V and H_K) for the crystal were found out at different loads. It is found that these numbers increase with increase in load. The Mayer's index *(n)* was found to be greater than 1.6 predicting soft-material natures. The fracture toughness value (K_C), was determined from measurements of crack length. The brittleness indices (B_i) were found for the grown crystals. Using Wooster's empirical relation, the elastic stiffness constant (C_{11}) was calculated from Vickers hardness values at different loads. Young's modulus was also calculated from Knoop microhardness values.

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Keywords: Microhardness number, Mayer's index, Fracture toughness, Brittleness indices, Elastic stiffness coefficient, Young's modulus

1. Introduction

In the modern world, the development of science in many areas has been achieved through the growth of single crystal. Nonlinear optical (NLO) materials are expected to play a major role in the technology of photonics including optical information processing, telecommunications, optical storage, etc. The organic nonlinear optical (NLO) materials have good NLO susceptibilities and electro-optical susceptibilities but low laser damage threshold value in comparison with inorganic counterparts. The organic compounds with polarized π conjugation systems have been found to have potential to exceed inorganic compounds [1]. So, in order to satisfy the day to day technological requirements, new NLO materials are mandatory to satisfy the requirements including telecommunications, optical computing, optical data storage and optical information processing [2]. The potential development of optoelectronic devices based on the nonlinear polarization of molecular materials has aroused much recent interest [3-4]. The search for large second order electric susceptibilities has concentrated on centric organic or organometallic chromophores with an organic π-electron system coupling electron donor and acceptor groups [5].The development of highly an efficient nonlinear optical (NLO) crystal for visible and ultraviolet regions is extremely important for both laser spectroscopy and laser processing. High- quality organic NLO crystals possesses sufficiently large nonlinear optical coefficient, wider optical transmission window coupled with shorter cut-off wavelength and low laser damage threshold power. However, most organic NLO crystals have usually poor mechanical and thermal properties, and it is difficult to grow large optical quality crystals of this class for device applications [6-9]. The measurement of hardness is very important as far as the fabrication of devices is concerned. In the present investigation, attention is focused on the mechanical properties of meta-Nitroaniline single crystals such as Meyer's index number, brittle index, fracture toughness and yield strength were calculated from Vicker's microhardness number (H_v). Young's modulus was calculated from the Knoop hardness.

2. Materials and methods

The starting material was commercially available as meta-Nitroaniline salt and its purity has been improved by recrystallizing in acetone for several times. The solvent evaporation technique was used to grow single crystals of meta-Nitroaniline.

A recrystallized salt was dissolved in acetone, a saturated solution was prepared and the solution was filtered using a borozil filter paper. The filtered solution was taken in a beaker which was hermetically sealed to avoid the evaporation of the solvent. A good yellow colored single crystal of meta-Nitroaniline was obtained in 20 days. The mechanical characterization of the meta-Nitroaniline crystals was analyzed by Vickers and Knoop microhardness studies at room temperature. Crystals with flat and smooth faces were chosen for the static indentation tests and the same crystal was mounted on the base of the microscope. The indentations were made gently by varying the loads from 10 to 100 g for a dwell period of 10 s using both Vickers diamond pyramid indenter and Knoop indenter attached to an incident ray research microscope (Mitutoyo MH112, Japan). The intended impression of Vickers was approximately square in shape. The shape of the impression is dependent on the structure, face and materials used. After unloading, the length of the two diagonals was measured by a calibrated micrometer attached to the eyepiece of microscope. For each load, at least five well-defined indentations were considered and the average is taken as *d*. The Vickers hardness 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 µm and H_V in kg/mm^2. The Knoop indented impressions were approximately rhombohedral in shape. The average 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 µm and H_K is in kg/mm^2. Beyond 50 g of the applied load, crack initiation and fragmentation were observed. So the hardness test could not be extended beyond this load. The elastic stiffness constant (C_{11}) was calculated using Wooster's empirical relation as [10]

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

3. Results and discussion

3.1 Vickers microhardness test

Fig. 1 shows the variation of H_V as a function of applied loads ranging from 10 to 100 g. It is clear from the figure that H_V increases with increase in load. The Mayer's index number was calculated from the Mayer's law, which relates the load and indentation diagonal length.

$$P = kd^n \quad (4)$$

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

where *k* is the material constant and *n* is the Mayer's index (or work-hardening coefficient). The above relation indicates that H_V should increase with the increase P if n > 2 and decrease with P when n < 12. The '*n*' value was determined from the plot of log P vs log d and the value was found to be 2.89 which is greater than 2 (Fig. 2). According to Hanneman [11] the values of '*n*' is less than 2 for hard materials and more than 2 for soft ones. Thus meta-Nitroaniline crystals belong to the soft-material category. The resistance pressure is defined as a minimum level of indentation load (W) below which there is no plastic deformation [12]. Hays and Kendall proposed a relationship between indentation test load and indentation size to calculate *W* by the equation

$$W = k_1 d^n - k_2 d^2 \quad (6)$$

(or)

$$d^n = \frac{W}{k_1} + \left(\frac{k_2}{k_1}\right) d^2 \quad (7)$$

The plot of d^n vs. d^2 is a straight line (Fig. 3) having slope k_2/k_1 and intercept W/k_1. From these values, *W* was calculated as 2.23 g.

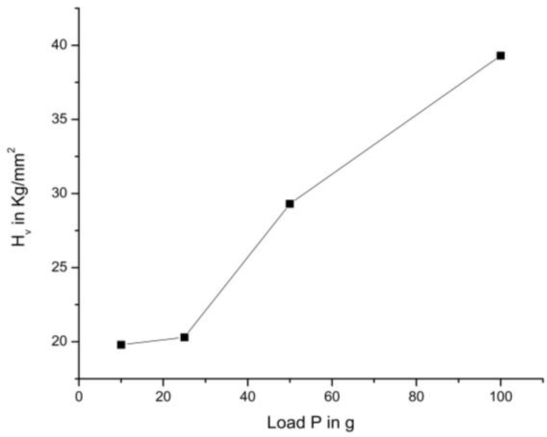

Fig. 1. Variation of the microhardness number H_V with load.

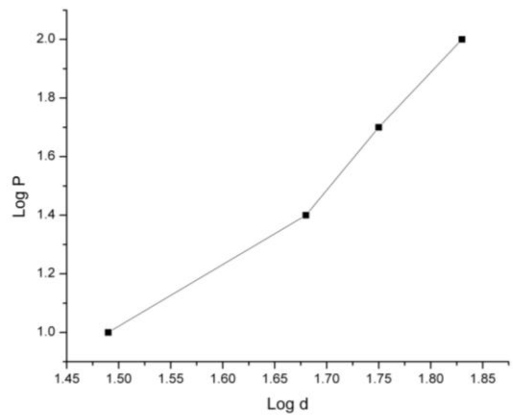

Fig. 2. log P vs. log d.

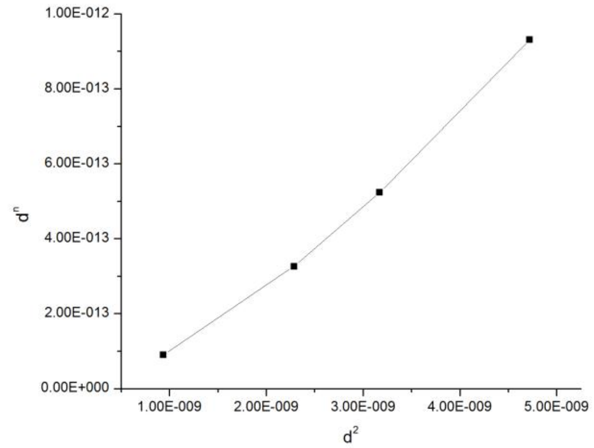

Fig. 3. Plot of d^n vs.d^2.

The elastic stiffness constant (C_{11}) was calculated by Wooster's empirical relation. The calculated stiffness constant for different loads were tabulated (Table 1). Crack length is measured from the centre of indentation mark to the crack end. Here the crack length (*l)* is the average of two crack lengths for each indentation. Resistance to fracture indicates the toughness of material [13]. The fracture mechanics of the indentation process gives an equilibrium relation for a well-developed crack extending under the centre loading condition

$$K_c = \frac{P}{\beta_0 l^{3/2}}, l \geq \frac{d}{2} \quad (8)$$

where β_0 is the indenter constant, equal to 7 for Vickers diamond pyramid indenter [14] and other symbols have their usual meanings. For the meta-Nitroaniline crystal the value of K_c is found to be 2.387×10^4 kg m$^{-3/2}$ and 7.095×10^4 kg m$^{-3/2}$ at 10 g and 100 g respectively.

Table 1.Elastic stiffness constant of meta-Nitroaniline.

H_V (Kg/mm^2)	$C_{11 \times 10^{14}}$ Pa
19.8	1.85
20.3	1.94
29.3	3.68
39.3	6.16

Brittleness is another property which affects the mechanical behaviour of a material and is expressed in terms of brittleness index (B_i) as.

$$B_i = \frac{H_V}{K_c} \quad (9)$$

The calculated values of B_i are found as 8.294×10^4 m$^{-1/2}$ and 5.538×10^4 m$^{-1/2}$at 25 g and 50 g respectively.

3. 2 Knoop microhardness test

Knoop hardness (H_K) was plotted against and load (P). The plot is shown in Fig. 4. From this measurement, it is found that as the load increases the Knoop microhardness number also increases. From the Knoop microhardness measurements, the Young's modulus (E) of the crystal was calculated using the relation [15].

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

where H_K is the Knoop microhardness values at a particular load, and b and a are the shorter and longer Knoop indentation diagonals respectively. The calculated Young's Modulus is 1.33×10^{10} Nm^{-2}.

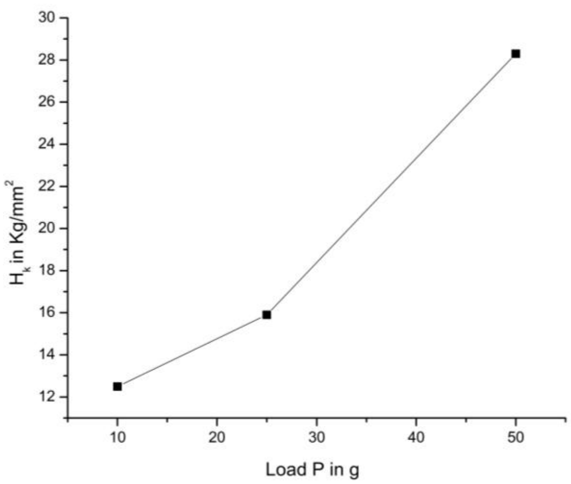

Fig. 4. Variation of the knoop microhardness with load.

4. Conclusion

The Vicker's and Knoop microhardness studies were carried out on the grown meta-Nitroaniline single crystal. The Vickers and Knoop hardness numbers were calculated for meta-Nitroaniline single crystal by the application of load and the hardness numbers were found to increase with increase in load. The value of the Mayer's index number is found as 2.89, which proves that meta-Nitroaniline falls in the soft-material category. Using Hays and Kendall's theory of resistance pressure, the minimum load needed to initiate the plastic deformation in the surface was calculated as W = 2.23 g. The calculation of the stiffness constant (C_{11}) reveals that the binding force between the ions is quite strong. The Young's modulus was calculated from the diagonal lengths of Knoop indentation.

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