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Influence of pH on the Mechanical Properties and Surface Analysis of L-threonine Single Crystals

Hanumantha Rao Redrothu, S.Kalainathan*

School of Advanced Sciences, VIT University, Vellore, Tamilnadu – 632014, India.

Corres.author: kalainathan@yahoo.com
Phone: + 91- 416 -2202350, Fax: 0416- 2243092.

Abstract: The crystal L-threonine grown by slow evaporation technique at various pH has been subjected to micro-hardness studies and chemical etching. The Meyer's index (n), yield strength (σ_{v}), and elastic stiffness constant (c_{11}) were calculated using Vicker's micro- hardness number.Microhardness studies revealed that the hardness of the grown crystal increases with an increase in load. From Meyer's index number it was found that material belongs to soft material category. It has been observed that L-threonine at isoelectric pH shows good mechanical strength. The Young's modulus has been estimated by Knoop's micro-hardness number. The surface of the grown crystals can be analyzed by chemical etching using water and methanol as an etchant. The results have been discussed in detail.

Keywords: Crystal growth, defects, elastic properties, mechanical properties, .surface properties.

1. Introduction

The growth rate of different crystal faces are relative to number of experimental parameters such as pH values, solvent saturation, temperature etc.The impact of pH on the thermal, electrical thermo mechanical properties and crystallization kinetics of L-threonine single crystals have been studied by Ramesh Kumar *et al.* [1, 2]. The present investigation deals with pH influence on mechanical properties and surface analysis of L-threonine single crystals. L-threonine ($C_4H_9O_3N$) is one of the naturally occurring amino acids which have been demonstrated to exhibit SHG efficiency 1.15 times greater than KDP [3]. It crystallizes in orthorhombic crystal system with the non-centrosymmetric space group P_{212121} .The unit cell parameters are a=13.610A^o, b=7.733A^o, c=5.147A^o [3].

2. Materials and methods

Commercially available L-threonine (Sigma Aldrich) was used for the growth procedure. A known amount of salt after successive recrystallization is mixed in 150ml de-ionized Millipore water is prepared according to the solubility data [3].The concentrated solution is filtered with high quality (whatman) filter papers and the solution is distributed in to three different beakers. The pH values of the concentrated solutions were adjusted to be 4.40, 5.87 and 6.70 using dilute acetic acid. After 12 days good quality seed crystals of L-threonine at various pH were taken from slow evaporation technique from the saturated solutions were obtained as shown in **Fig.1.**

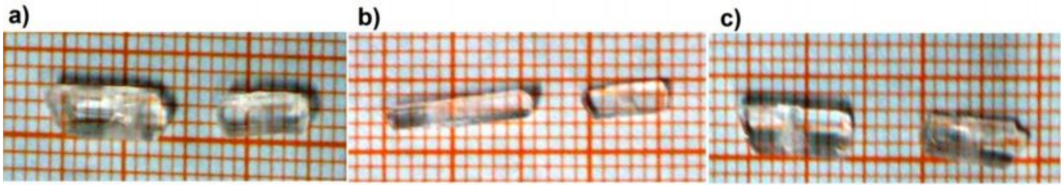

Fig .1 ***As grown crystals of L-threonine at pH a) 4.40 b) 5.87 and c) 6.80.***

The mechanical studies of l-threonine single crystals at various pH were made by Vicker's and Knoop's hardness microhardness tests ay room temperarure.Crystals, free from cracks, with flat and smooth faces, were choosen for the static indentation tests. The crystal was mounted properly on the base of the microscope. Now, the selected faces were indented gently by loads varying from 10 to 50 g for a dwell period of 10s using both Vicker's diamond pyramid indenter and knoop's indenter attached to an incident ray research microscope (Mututoyo MH 112, Japan).The Vicker's 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 and the average was found out. For a particular load at least five well defined indentations were considered and the average of all the diagonals (d) was considered. The H_v was calculated using the standard formula:

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

Where P is the applied load in kg, d is in mm and H_v is in $Kgmm^{-2}$.

The knoop indented impressions were approximately rhombohedral in shape. The average diagonal length (d) was considered for the calculation of the knoop microhardness number (H_k) using the relation

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

Where P is the applied load in kg, d is in mm and H_k is in $Kgmm^{-2}$.

Crack initiation and fragmentation become significant beyond 50g of the applied load. So hardness test could not be carried out above this load. From Wooster's empirical relation [4],

$$c_{11} = H_v^{7/4} \qquad (3)$$

Elastic stiffness constant of L-threonine at various pH was estimated. This value gives an idea about the tightness of bonding between neighboring atoms. From the hardness value the yield's strength σ_v of a material is calculated from the relation [5],

$$\sigma_v = \frac{H_v}{2.9}\left\{[1-(n-2)] \times \left[\frac{12.5\,(n-2)}{1-(n-2)}\right]^{n-2}\right\} \qquad (4)$$

In order to know the quality of the grown crystals, the etching technique that uses water and methanol of the above solvents as an etchant was used. Etchings of the surfaces were carried out by dipping the plates for 10 sec at room temperature and then wiping them with dry filter paper. Etch patterns was observed and photographed under an optical (Olympus BX 61, Japan) microscope in reflected light. In order to know the quality of the grown crystals, the etching technique that uses water and methanol of the above solvents as an etchant. For etching purpose thin plates of 5mm thickness of the face along c-axis were cutout from the grown crystal with the help of wet thread. Polished plates which are free from visible inclusions or cracks were selected for etch pit study.

Etchings of the surfaces were carried out by dipping the plates for 10 sec at room temperature and then wiping them with dry filter paper. Etch patterns were observed and photographed under an optical (Olympus BX 61, Japan) microscope in reflected light.

3. Results and Discussion

3.1 Vickers Microhardness test

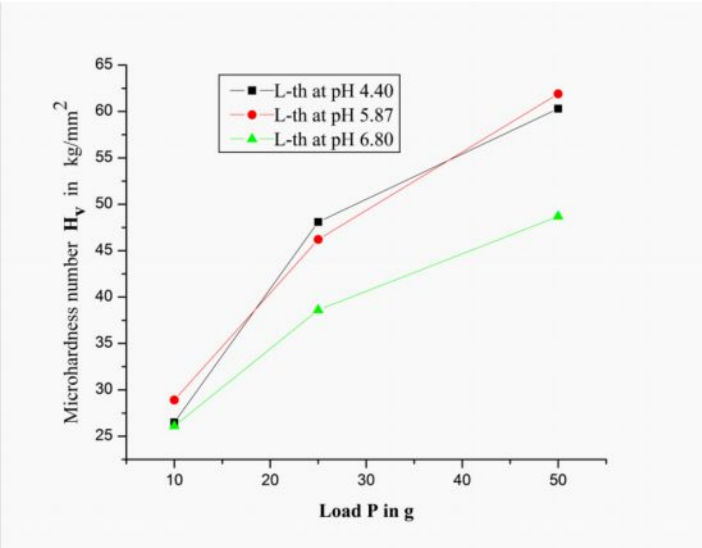

Fig .2 ***Variation of Vickers microhardness number H_v with load***

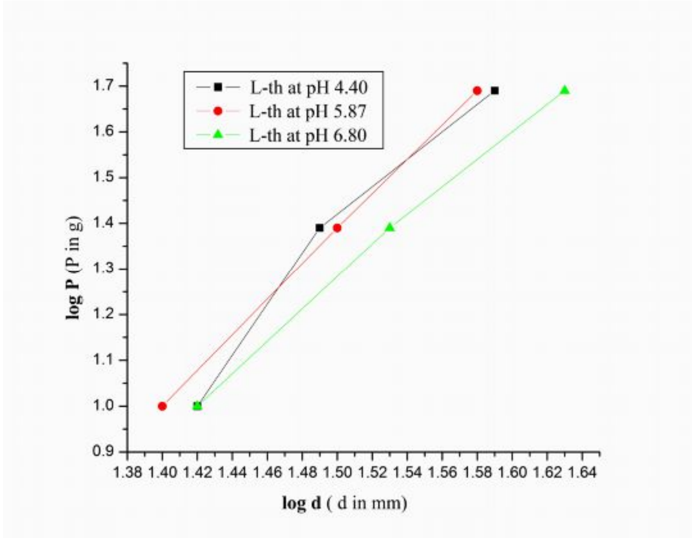

Fig .3 ***Graphs between log P verses log d***

Fig.2 shows the variation of H_v as a function of applied load ranging from 10g to 50g at various pH for the L-threonine single crystals .It is very clear that L-threonine at isoelectric pH [1] at a load of 10g and 50g shows slightly high hardness value. The Meyer's index number was calculated from the Meyer's law, which relates the load and indentation diagonal length as $P = kd^n$

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

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

In order to find the value of 'n', a graph is plotted for log P against log d (Fig.3) at various pH which gives a straight line. From the slope of each line the Meyer's index number 'n' at pH 4.40, 5.87, 6.80 was calculated to be 3.98, 3.83, 3.29 respectively.

From the literature [4, 6], H_v should increase with the increase of P if n>2 and decrease if n<2.The 'n' value agrees well with the experimental data (Fig .2). According to Onitsch 'n' should lie between 1 and 1.6 for harder materials and above 1.6 for softer materials [4]. Thus L-threonine at all mentioned pH falls in soft material category.

The elastic stiffness constant (c_{11}) at various pH 4.40, 5.87, 6.80 was calculated using Wooster's empirical formula (eqn.3). The calculated stiffness constant for load at 10g are 5.31, 6.19 and 5.18 x 10^{14} Pa respectively.

From the Hardness value the calculated Yield strength σ_v (eqn.4) of L-threonine at pH 4.40, 5.87, 6.80 for load at 10g are 86.6, 91.5 and 85.3MPa respectively.

3.2 Knoop microhardness

The graph was plotted against Knoop hardness (H_k) and load (p).The plot is shown **in Fig.4.** From this measurement, it was found that only at the pH 5.8 as the load increases up to 50g, the knoop microhardness number also increases as like Vickers microhardness which is due to the reverse indentation size effect [10].From the Knoop microhardness measurements the Young's modulus (E) of the crystal at pH 4.40, 5.87, 6.80 for 10g load was calculated using the relation [9],

$$E = 0.45H_k / (0.1406 - b/a) \cdot \quad (6)$$

Where H_k is Knoop microhardness values at a particular load, and b and a are the shorter and longer Knoop indentation diagonal respectively.

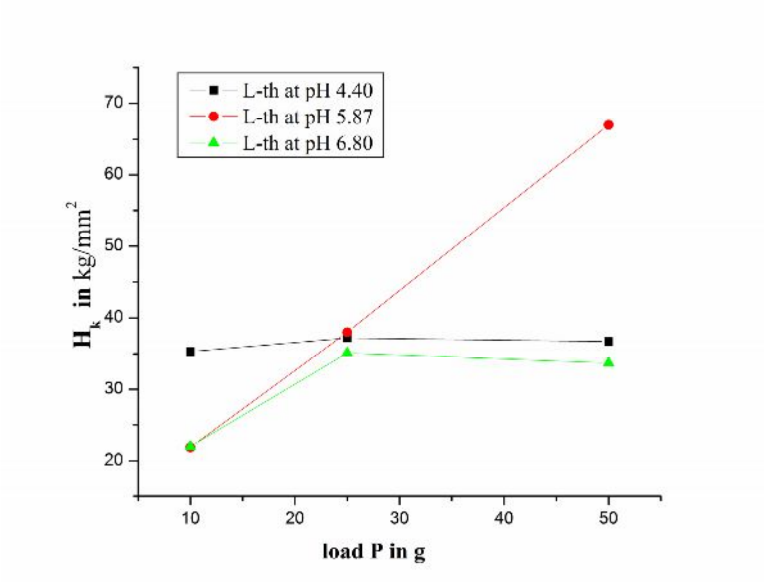

Fig.4 Variation *of Knoops microhardness number H_k with load*

The calculated Young's modulus for 10g at pH 4.40, 5.87, 6.80 is 1.011 x 10^{10}, 0.3025 x 10^{10} and 0.2533 x 10^{10} Nm^{-2} respectively.

3.3 Chemical etching

To investigate the perfection of crystalline samples, etching studies are done on grown L-threonine single crystals at PH 4.40, 5.87, 6.80 using water and methanol as an etchant. Natural etching of crystals has been reported in case of wide variety of natural crystals [7, 8].

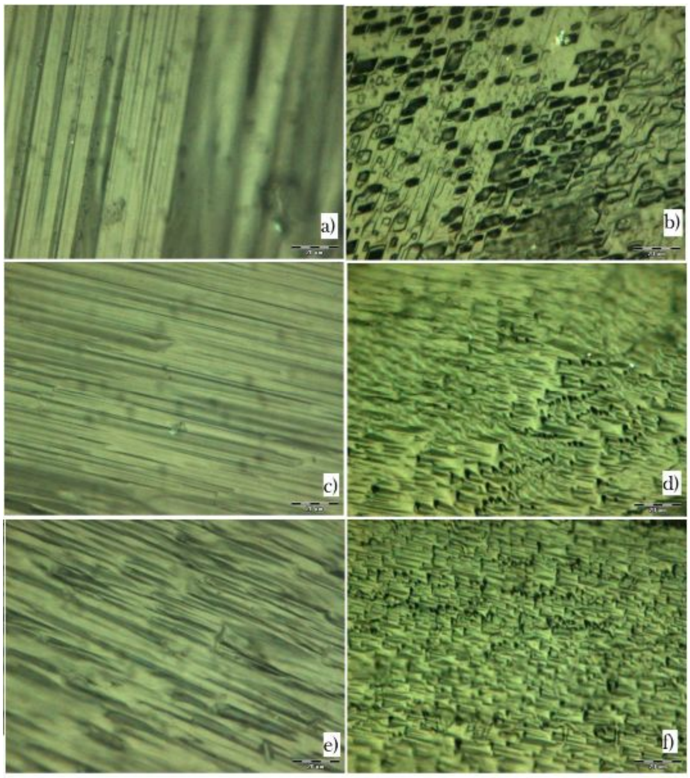

Fig.5 ***Etch patterns produced on grown L-threonine at pH 4.40, 5.87and 6.80 using water (a, c, e) and methanol (b d f).***

In (Fig. 5a, c, e) elongated deep striations were observed. The etch pits in Fig.5b shows rectangular in shape having elongation perpendicular to c-axis. It is evident from Fig.5d and Fig.5f two types of pits are produced on the etched surface. The dislocation density from Fig.5f is more as shown from Fig.5d. The etch pits from Fig5b shows layer growth which shows the crystal of L-threonine grows in a two- dimensional nucleation mechanism.

4. Conclusion

Mechanical properties and surface analysis of L-threonine single crystals have been examined at various pH values. The crystal grown at isoelectric pH shows greater values in stiffness constant and yield strength. The value of Meyer's index at all pH shows the material falls in to soft material category. The greater value of stiffness constant at isoelectric pH shows that binding force between the ions is very strong. Also the young's modulus was calculated from diagonal lengths of knoop indentation. Etching studies reveals that at isoelectric pH the dislocation density is low which indicates higher crystal perfection. So at low pH at 4.40 or at high pH 6.80 it is disadvantageous to grow L-threonine single crystals.

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