EVALUATION OF STIFFNESS CONSTANT C_{11} AND YIELD STRENGTH (σ_v) OF SOLUTION GROWN SEMI ORGANIC NONLINEAR OPTICAL CRYSTALS

M. N. RAVISHANKAR[a,b*], R. CHANDRAMANI[b], A.P. GNANAPRAKASH[a]
[a]*Department of Physics, PG studies, Manasagangatori, University of Mysore, India*
[b]*Department of Physics, Dayananda sagar college of Engineering, Bangalore, India*

Synthesis, Growth and characterization of NLO crystals especially semi organic materials has become a sizzling field of research in present day technology. Here an attempt has been made mainly to evaluate mechanical properties, like Vicker's micro hardness number (H_v), Stiffness constant (C_{11}) and Yield strength (σ_v) of solution grown semi organic nonlinear optical (NLO) crystals. These NLO crystals will retain the merits of organic and inorganic material, like SHG response and flexibility of organic and good hardness of inorganic materials.

(Received August 1, 2011; accepted December 16, 2011)

Keywords: Semi organic, Mayer's index, Yield strength, stiffness constant NLO

1. Introduction

Non linear optics has emerged as one of the most attractive fields of current research in view of its vital application in areas such as optical modulation, optical logic, frequency shifting, optical switching and optical data storage. Glycine is the simplest of all amino acids among the organic materials. It has been reported that some complexes of amino acids with simple inorganic salts may exhibit ferroelectric properties [1-3]. Semi organic non linear optical crystals have large mechanical strength and chemical stability compared with organic crystals. It is difficult to grow large size, high quality crystals. The challenge faced by researchers in this emerging field is the identification of new types of functional materials by rational construction of molecular assemblies exhibiting nonlinear optical effects. In addition to that the task is the fulfillment of secondary requirements such as thermal, mechanical and chemical stabilities [4]. Various strategies are being carried out by the researches to bring out the suitable materials such as formation of metal complexes and salts or introduction of steric effects and hydrogen bonding interactions [5]. In the present study we have made an attempt to grow number of semi organic non linear optical crystals of γ-Glycine(G), L-Leucine with additives. Ammonium Oxalate (AO), Barium Nitrate (BN) and Potassium Nitrate (PN) are used as additives by aqueous solution method. We mainly focus on mechanical characterization of all grown crystals. Since micro hardness has direct correlation with the crystal structure and is sensitive to lattice perfection, inter atomic spacing [6], mechanical properties have been studied employing Vicker's micro hardness tester. Various hardness parameters namely, micro hardness (H_v), Mayer's Index (n), yield strength (σ_v) and elastic stiffness constant (C_{11}), have been estimated for all the grown samples.

* Corresponding author: ravibhumi2004@gmail.com

2. Experimental

All the crystals were grown in slow evaporation method. Good transparent crystals were obtained in a matter of 3 to 4 weeks. Fig-1, Fig-2, Fig-3, and Fig-4 show all the crystals. The crystals were characterized on the basis of XRD, FTIR, UV-Vis-IR measurements. The above crystals have been studied their second harmonic generation (SHG) efficiency [7].

Fig-1 LLeucinePN crystal.

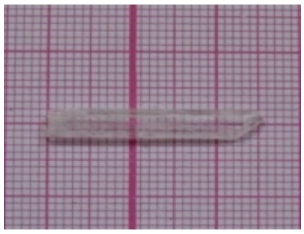

Fig-2 GAO Crystal.

Fig-3 GBNPN Crystal.

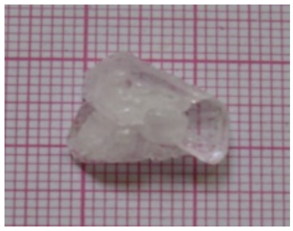

Fig-4 L-Leucine BN crystal.

3. Mechanical characterization

In order to understand the plasticity of the crystals, micro hardness tests were carried out on the grown crystals. The hardness of the crystals depends on type of chemical bonding, lattice energy, Debye temperature, heat of formation and interatomic spacing [6], which may differ along the crystallographic directions. The hardness test for grown NLO crystal was carried out by M H-5 hardness tester. The diagonal length of their indentation with various applied loads in grams is measured for a constant indentation period of 10 seconds. The Vicker's micro hardness number (H_v) is calculated using the relation [8].

$$H_v = \frac{1.8544\,P}{d^2}\ \text{N/mm}^2$$

where P is applied load in Newton and d is diagonal length of the indentation in mm. The variation of H_v with the applied load P for all the crystals are shown in Fig- 5, Fig- 6, Fig- 7, and Fig- 8. Plots of logP versus log d for the grown crystals are shown in Fig- 9, Fig- 10, Fig- 11, and Fig- 12.

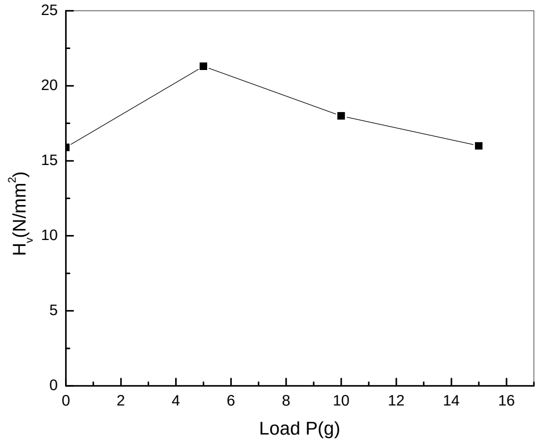

Fig-5 Variation of H_v versus Load P for L-LeucinePN Crystal.

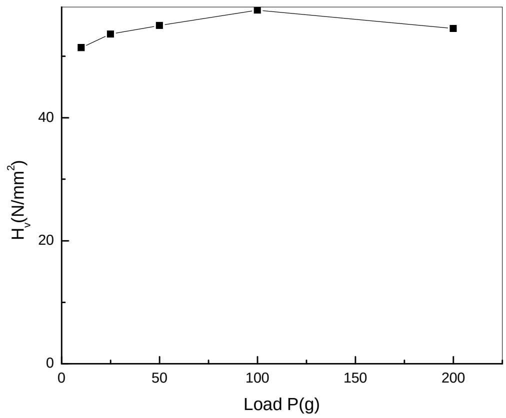

Fig-6 Variation of H_v versus Load P for GAO Crystal.

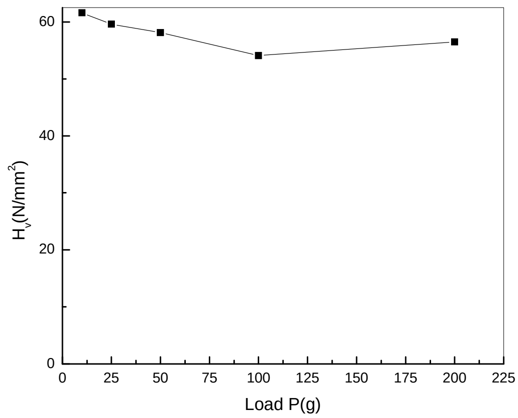

Fig. 7 Variation of H_v versus Load P for GBNPN Crystal.

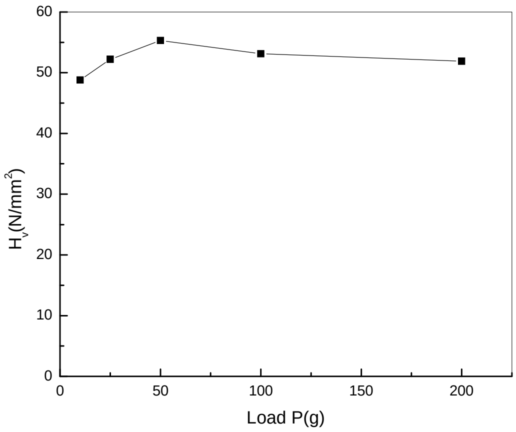

Fig. 8 Variation of H_v versus Load P for L-Leucine BN Crystal.

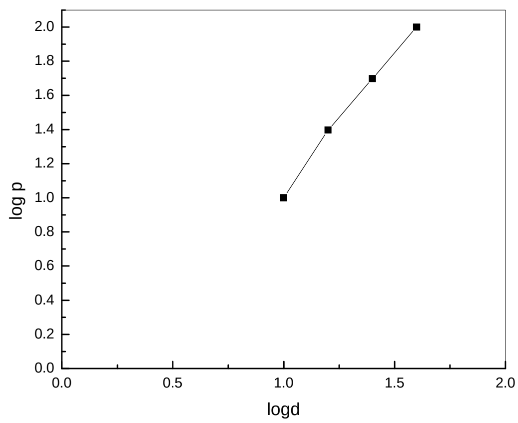

Fig. 9 Log p vs log d of L-LeucinePN Crystal.

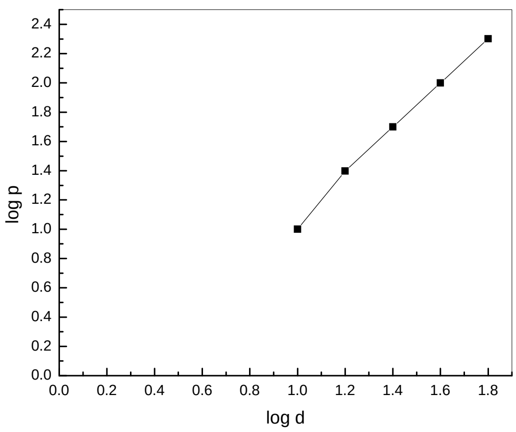

Fig. 10 Log p vs log d of GAO Crystal.

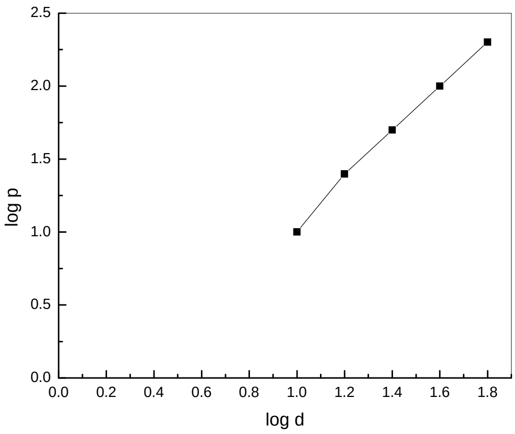

Fig. 11 Log p vs log d of GBNPN Crystal.

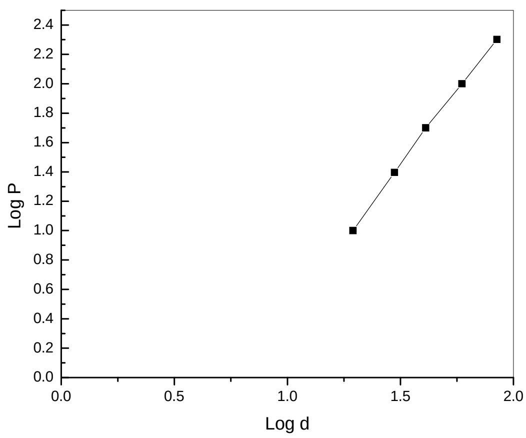

Fig. 12 Log p vs log d of L-Leucine BN Crystal.

The plot of logP versus log d is a straight line and its slope gives work hardening index n given in Table-1.

Table. 1 Work Hardening index n.

Grown Crystal.	Work Hardening Index n.
L-Luecine Potassium Nitrate.	1.61
Glycine Ammonium Oxalate.	1.816
GlycineBarium Nitrate Potassium Nitrate.	1.853
L-Leucine Barium Nitrate.	2.00

From the hardness value, the yield strength (σ_v) can be calculated using the relation,

$$\sigma_y = \frac{H_v}{2.9}\{1-(2-n)\}\left[\frac{12.5(2-n)}{1-(2-n)}\right]^{2-n}$$

The yield strength σ_v were calculated for grown crystals and are given in the Tables 2, 3,4and 5.

Table. 2 Yield strength (σ_v) of the L-Leucine P N crystal.

Load P in grams.	σ_v M pa
10	7.67
25	10.28
50	8.689
100	7.724

Table. 3 Yield strength (σ_v) of the Glycine Ammonium Oxalate crystal.

Load P in grams.	σ_v M pa
10	17.364
25	18.04
50	18.726
100	19.40
200	18.38

Table. 4 Yield strength (σ_v) of the GBNPN crystal.

Load P in grams.	σ_v M pa
10	20.28
25	19.622
50	19.1289
100	17.811
200	18.60

Table. 5 Yield strength (σ_v) of the L-Leucine crystal.

Load P in grams.	σ_v M pa
10	20.02
25	21.78
50	23.07
100	22.11
200	21.65

The elastic stiffness constant (C_{11}) were calculated for all the grown crystals using Wooster's empirical relation as $C_{11} = H_v^{7/4}$ [9 and 10]. The calculated stiffness constant for a load from 10gms to 200 gms have been calculated and are given in Tables 6, 7, 8, and 9. We have got a moderate value of C_{11}, which indicates that the binding forces between the ions are quite strong.

Table. 6 Stiffness constant of L-Leucine Potassium Nitrate crystal.

Load P	$H_v(N/mm^2)$	$C_{11} \times 10^{14}$ Pa
10	15.9	1.26
25	21.3	2.11
50	18.00	1.57
100	16.00	1.28

Table. 8 Stiffness constant of Glycine Barium Nitrate Potassium Nitrate crystal.

Load P	$H_v(N/mm^2)$	$C_{11} \times 10^{14}$Pa
10	61.6	13.54
25	59.6	12.78
50	58.1	12.22
100	61	13.31
200	56.5	11.64

Table-7 Stiffness constant of Glycine Ammonium Oxalate crystal.

Load P	$H_v(N/mm^2)$	$C_{11} \times 10^{14}$Pa
10	51.4	9.86
25	53.6	10.61
50	55	11.1
100	57.5	11.82
200	54.5	10.93

Table. 9 Stiffness constant of L-Leucine Barium Nitrate crystal.

Load P	H_v(N/mm^2)	C_{11} x 10^{14}Pa
10	48.8	9.01
25	52.2	10.13
50	55.3	11.21
100	53.0	10.41
200	51.9	10.03

4. Conclusions

Good quality transparent crystals were obtained in 3-4 weeks.

All the grown crystals were subjected to single crystal XRD, FTIR, SHG.

Various hardness parameters n, H_v, σ_v, C_{11} have been estimated from micro hardness measurement up to a load 200g using Vicker's micro hardness tester.

L-Leucine Barium Nitrate crystal possesses favorable yield strength (σ_v) and Glycine Barium Nitrate Potassium Nitrate crystal possesses favorable stiffness constant (C_{11}).

Acknowledgements

The Authors thanks to Head of the department, Mechanical division, HAL, Bangalore for providing micro-hardness test facilities. Authors are grateful to the management, DSCE, Bangalore-78 for their constant support and encouragement.

References

[1] R. Pepinsky, Y. Okaya, D.P. Eastman, and T.Mitusui, Phys.Rev., **107**, 1538, (1957)
[2] R. Pepinsky, K.Vedam, and Y. Okaya, Phys.Rev. , **110**, 1309, (1958**)**
[3] A. Deepthy, and H.L. Bhat, J. Cryst, Growth, **226,** 287 (2001)
[4] C. Chen, N. Ye, J.Lin, J. Jiang, W. Zing, B.Wu, Adv.Matter., **11**(13)**,** 1071**(**1999**)**
[5] D. S. Chemla, J.Zyss, Nonlinear optical properties of organic molecules and crystals, Academic press, Orlando, **Vol.1/2**. (1987**)**
[6] Jiaghong, Gong, J. Mater. Sci. Lett., **19**, 515 (2000)
[7] M N Ravishankar, R Chandramani, A.P. Gnanaprakash, Int.J. ChemTech Res., **3(3),** (2011)
[8] B. W. Mott, "Micro indentation hardness tests", (1957).
[9] W. A. Wooster, Rep. Progr. Phys**.,** **16**, 62. **(**1953)
[10] R. Ezhil Vizhi, D. Rajan Babu, K. Sathiyanarayanan, Ferroelectrics let. sec., **37**(2), 23 (2010)