LOAD DEPENDENCE OF THE MEASURED HARDNESS ON SOME GLYCINE BASED NON-LINEAR OPTICAL CRYSTALS

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Abstract: *The Vickers microhardness on as-grown faces of glycine potassium nitrate (GPN), glycine hydrofluoride (GHF), bisglycine hydrogen chloride (BGHC), glycinium oxalate (GOX) and glycine lithium sulphate (GLS) crystals was measured in the indentation load ranging from 10 to 100 g. It was found from the load-hardness curves that the crystals exhibit indentation size effect (ISE). Meyer's law was used to understand the relationship between the load and the size of indentation. An empirical relation was derived between the constants. It can be inferred that Meyer's law is consistent in distinguishing between normal and reverse ISE.*

Keywords: Crystal growth; Microhardness; Indentation; Meyer's law

1. Introduction

The detailed investigation of the deformation characteristics has become quite essential for the development of new materials for industrial applications (opto-electronics, ferro-electrics, piezo-electrics, etc.) as in some of these applications; the materials undergo constant mechanical stress and thereby needs mechanical stability. To assess the mechanical properties of crystalline and non-crystalline solids, microindentation hardness testing is widely used, which provides information on the strength and deformation characteristics. In this testing method, the hard tip of an indenter is pressed under a fixed load into the material. The hardness is then estimated from the ratio of the applied load to the pyramidal contact area (for Vickers indenter) on the specimen.

Generally, the size of indentation varies with the applied load, and is known as indentation size effect (ISE). The trend of decrease in hardness with the increasing load is termed as normal ISE. This type of load variation of hardness has been observed by several researchers [1-4] to list a few. In contrast to the normal ISE, a reverse type of ISE (termed reverse ISE), where the hardness increases with increasing load, is also observed. This trend in load dependence is also observed by the researchers [5-9], mostly in the last two decades. The normal ISE and reverse ISE are illustrated schematically in Figure 1a and 1b respectively. In addition to these, hardness was found to increase and then decrease (Figure 1c) for PbS [10] and $SrLaAlO_4$ (SLA) and $SrLaGaO_4$ (SLG) crystals [11]. In the case of $GdCa_4O(BO_3)_3$ crystal, the hardness initially decreases and then increases with the applied load (Figure 1d) [12]. Further, there are some reports in the literature where hardness value does not attain saturation (load independent) region, but continuously either increases or decreases.

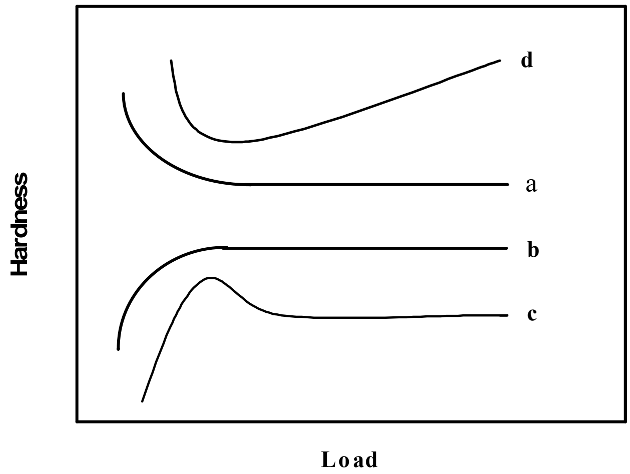

Figure 1: Types of load variation of hardness.

As mentioned earlier, hardness is one of the important parameters for non-linear optical crystals for their practical applications. Hence, the purpose of this article is to study the load-hardness curves for some semiorganic non-linear optical crystals viz**.** glycine potassium nitrate (GPN), glycine hydrofluoride (GHF), bisglycine hydrogen chloride (BGHC), glycinium oxalate (GOX) and glycine lithium sulphate (GLS) and thereby understand the load dependence of hardness through Meyer's law.

2. Experimental

2.1 Crystal growth

For the growth work, known amounts of salts based on the stiochiometric ratio (shown in Table 1) were taken and dissolved in deionized double distilled water. The solution was stirred well (for at least 5 h) and saturated solutions of about 500 ml were prepared in each case. These saturated solutions were taken in beakers and allowed for slow evaporation at 35^{o}C in a constant temperature bath. Good quality crystals were obtained in a period of 10 to 15 days. The average growth rates along the longer edge (major direction) for these crystals are presented in Table 1.

Table 1: Composition and growth rates of the crystals.

S.No.	Crystal	Composition of salts	Growth rate (along the longer edge)
1	Glycine potassium nitrate (GPN)	Glycine and Potassium nitrate (1:1)	1.5 mm/day
2	Glycine hydrofluoride (GHF)	Glycine and Hydrofluoric acid (1:1)	1.1 mm/day
3	Bisglycine hydrogen chloride (BGHC),	Glycine and Hydrochloric acid (2:1)	1.3 mm/day
4	Glycinium oxalate (GOX)	Glycine and Oxalic acid (1:1)	0.32 mm/day
5	Glycine lithium sulphate (GLS)	Glycine and Lithium sulphate (1:1)	0.26 mm/day

2.2 Microhardness measurement

Microhardness measurements were made using Leitz-Wetzlar (miniload 2) microhardness tester equipped with a Vickers diamond pyramidal indenter. The samples with smooth plane surfaces were chosen and loads ranging from 10 to 100 g were used with a constant indentation time of 15 sec in all cases. Hardness values H_v are estimated from the expression,

$$H_v = 1.854(P/d^2) \text{ kg/mm}^2 \quad (1)$$

where P is the load applied on the indenter in g and d is mean diagonal length of the square impression formed on the crystal surface in µm.

3. Results and Discussion

3.1 Load variation of hardness

The plots of hardness against applied load on (220) GPN, (110) GHF, (012) BHGC, (110) GOX, and (001) GLS crystals are shown in Figure 2. It can be seen that the hardness values for GOX, BGHC, GLS crystals increases initially at low loads (upto 35g) then attain saturation values exhibiting reverse ISE. For GPN crystals, the hardness value decreases with applied load upto 35g then attains load independent hardness value exhibiting normal ISE. Whereas, in case of GHF, the hardness value increases up to a load of 25g with further increase in applied load, it decreases till 50g and then attains a load independent value showing both ISEs. The load independent hardness values are listed in Table 2.

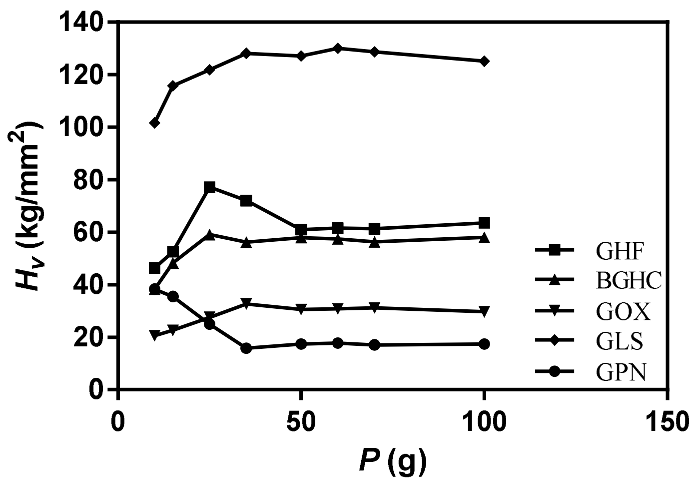

Figure 2: Load-hardness curves for the crystals under study.

3.2 Meyer's law

The simplest description of ISE was expressed by Meyer's law [13,14], which gives a relationship between load and size of indentation. It is expressed as,

$$P = Ad^n \quad (2)$$

where the exponent n is called as Meyer index (or work hardening coefficient) and A is a constant for a given material. Equation 2 can be written as

$$\ln P = \ln A + n \ln d \quad (3)$$

'n' is the value obtained from the plots of linear regressions between ln P vs ln d The exponent n usually is < 2 and > 2 for crystals exhibiting normal and reverse ISE. When $n = 2$, the hardness is independent of the applied test load and is given by Kick's law [13,14],

$$P = A_o d^2 \quad (4)$$

where A_o is a geometric conversion factor for the Vicker indenter and $A_o = 1854$. The plots of ln P versus ln d for the crystals under study is shown in the Figure 3, represented as a single plot in the entire range of load *P*. The estimated values of *n* and ln *A* with a corresponding correlation coefficient (CC) for the best fit data are given in Table 2. It can be observed from this table that $n > 2$ for GHF, BGHC, GOX, GLS and $n<2$ for GPN crystals. However, plots are also drawn between ln *P* and ln *d* for low loads ($d < d_c$) and high loads ($d > d_c$) which can be represented by two segments of plots, where d_c is the critical indentation diagonal length at which load independent hardness value is attained. The *n* values determined for both the ranges are shown in the table with a CC > 0.999. It is observed that at high loads, which is the load independent region, $n \sim 2$ which supports the Kick's law. Hence, it is concluded that Meyer's law is consistent for the present crystals under study and it clearly distinguishes between normal and reverse ISE based on the *n* value. However, through this law, one cannot explain the origin of ISE either based on the values of *n* or through any mechanisms dealing with elastic and plastic deformation.

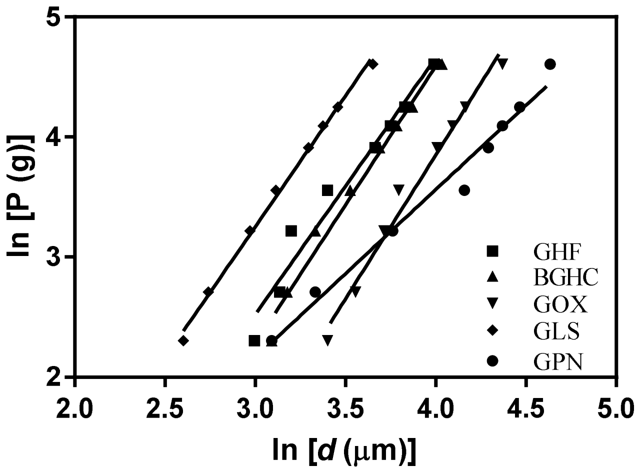

Figure 3: Plots of ln *P* vs ln *d*.

Table 2: Values of *n* and ln *A* for different crystals as calculated from Meyer's law.

Crystal [Ref.]	Plane	H_v (kg/mm^2)	*n* (entire range)	ln *A*	CC	n ($d<d_c$)	n ($d>d_c$)
GPN [15]	(220)	17	1.401	2.043	0.9800	1.239	1.947
GHF [16]	(110)	62	2.410	-3.900	0.9626	2.371	2.146
BGHC [17]	(012)	57	2.313	-4.661	0.9827	2.581	2.061
GOX [18]	(110)	42	2.395	-5.729	0.9820	2.763	2.073
GLS [19]	(001)	130	2.184	-3.300	0.9962	2.308	2.085

Further, the plot of *n* versus ln *A* (Figure 4) for all the crystals, clearly indicates that a sample possessing a higher value of *n* has a lower value of ln *A* and vice versa. This linear dependence is given by the relation

$$n = 1.013 - 0.3241 \ln A \quad (5)$$

with a CC equal to 0.7833. A similar dependence was observed by Sangwal et al. [20]. Equation 5 represents a general empirical relation between *n* and ln *A*, where 1.013 and 0.3241 are the empirical constants. It can be observed from the above equation that when $n = 2$, $A = 0.047$ g/μm^2. Based on the results obtained, it is reasonable to attribute that if the obtained value of A is less than 0.047 g/μm^2, reverse ISE and if it is more, then normal ISE is observed.

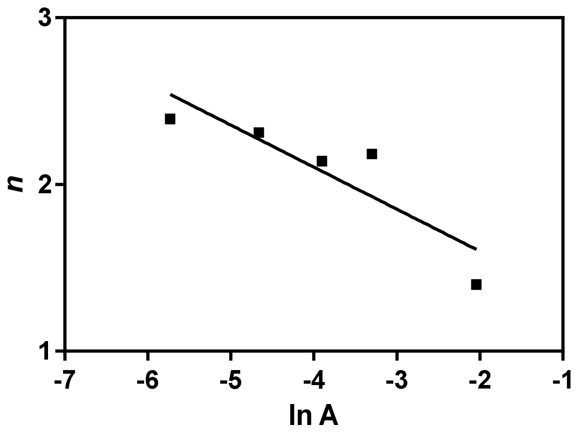

Figure 4: Plots of n versus ln A.

4. Conclusions

The load-hardness curves for the as-grown GPN, GHF, BGHC, GOX and GLS crystals indicate that except for GPN, all the other crystals exhibit reverse ISE. The plots between ln P and ln d indicate that wherever the CC is relatively less, the linear regression of plots fall into two segments. Meyer's law is consistent in distinguishing between normal and reverse ISE based on the n values from two segment plots, however, it does not provide the reasons for the origin of ISE. The value of n comes out to be 2 in the load independent region, validating the Kick's law. The plot of n versus ln A indicates that a sample possessing a higher value of n has a lower value of ln A and vice versa. With the available experimental data, it can be concluded that if the obtained value of A is less than 0.047 g/μm^2, reverse ISE is observed, otherwise normal ISE.

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