CHAPTER: 4

MICRO HARDNESS OF $InSb_{1-x}Bi_x$ (x=0, 0.03, 0.04, 0.05) CRYSTALS

I. INTRODUCTION

The most extensively used procedures for assessment of hardness of the valuable crystals both of metallic and nonmetallic nature is indentation method, and by applying this method on a small specimen different assessments can be finalized. This is the major advantage of this method. Indenters have been known to be either sharp or blunt according as their included angles are less or greater than 90°. As this angle increases, the indenter tends to be blunt and the influence of friction and prior strain hardening decreases. Also the value of constrain factor C in the relation between hardness and yield stress, i. e., H= CY, tends to 3 as effective cone angle increases (Shaw) [1]. The stress field produced by such an indenter closely approximates to the prediction of elastic theory. The Vickers diamond pyramidal indenter used in the present study has the included angle of 136° which is a good compromise to minimize frictional effect and at the same time to give a well-defined geometrical square shape to the indentation mark. The estimation of the indenter is shown under:

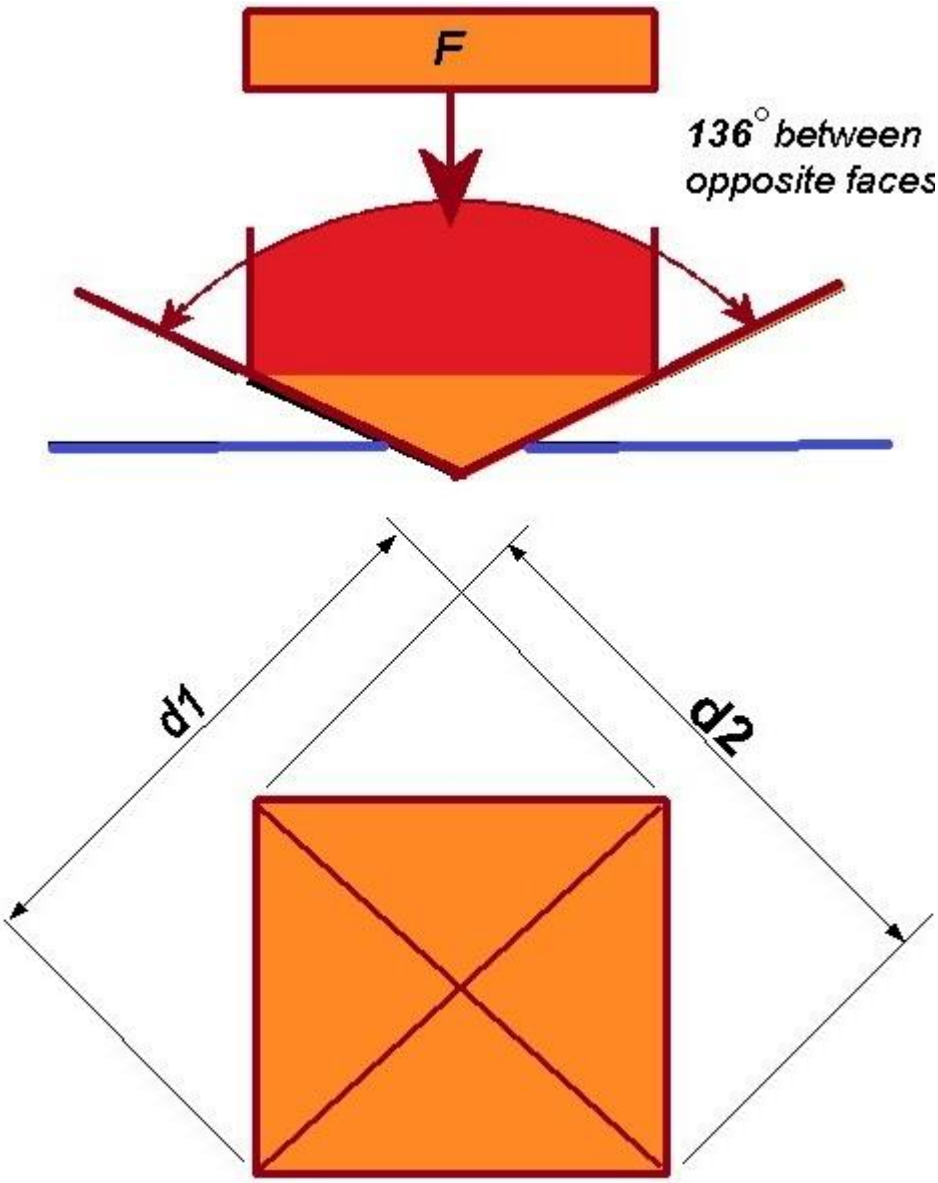

Figure-1 Vickers indentor

In like manner during the diamond contact with the cleavage surface of a metal, the coefficient of friction ranges from 0.1 to 0.15 having the frictional effects less expressed (Tabor) [2]. Vickers hardness is the ratio of applied load to the pyramidal contact area of indentation and represented as

$$H_v = \frac{1854 \times P}{d^2} \qquad (1)$$

where,

H_v = Vickers micro hardness in MPa

P = applied load in mN

d = mean diagonal length of the indentation mark in μm

The indentation mark is geometrically similar whatever its size. This would suggest the hardness be independent of load. This isn't the situation and except for load surpassing around 200 gm (for example 1960 mN) in general, the obtained hardness value has been found to rely upon load in practically all cases and consequently the hardness value measured in the low load region (<200gm. i.e., < 1960 mN), are known as micro hardness. However, the cutoff load isn't strongly characterized and essentially the hardness might accomplish a constant value for loads in the range 20 to 50 gm (i.e., 196 to 490 mN) and then some, as per material dependency.

As a rule, the idea of the variation of hardness with load is very intricate and doesn't observe any widespread guideline. Numerous researchers have concentrated on the load dependency of hardness and the outcomes got are very befuddling. Concerning the model, Bergsman noticed an exceptionally articulated load reliance of hardness [3]. Rostoker [4] investigated the load fluctuation of hardness in copper and found a reduction in hardness at low applied loads. Buckle [9], on the other hand, found that with low applied load, there is a considerable increase in hardness values. Due to elastic recovery after removing the applied force, which lessens the diagonal length, this increase in the hardness value has been observed, Grodzinsky [11] discovered that the plot of hardness against load for sintered carbides had a peak at low applied loads. The rise in hardness value with decreasing load was discovered by Knoop et al [5] and Bernhadt [6]. On the other hand, Campbell et al [7] and Mott et al [10] found that when the load was reduced, hardness decreased. Taylor [8] and Toman et al [12] found no noteworthy change in the hardness value as a function of load variation. The impact of the surface layers and vibrations during the process might explain the inconsistent results [5-13]. Gane et al [14] researched micro hardness under extremely low stresses. They noticed a major increase in the hardness at tiny indentation sizes, which they attributed to the high pressures necessary for homogenous nucleation of dislocations in the indented small dislocation free zones. Ivanko [15], on the other hand, discovered that as load lowers, micro hardness decreases,

and he theorised that this is owing to the proportionate contributions of indentation process' plastic and elastic deformations. According to these many views and reports, it is impossible to draw any definitive conclusions about the link between micro-hardness and applied load. To be independent of load P, the hardness should be exactly proportional to the square of the diagonal length "d," as indicated in equation 1. Thus,

$$P = ad^2 \qquad (2)$$

where “a” is a material constant. This equating is known as Kick’s law.

According to the above discussion, the hardness dependency on load indicates that the power index should vary from 2 and following Hanemann [16], the form of dependency of load on the diagonal length was be in the form

$$P = an \qquad (3)$$

Here, the dependence of hardness on load reflects in the deviation of the value of the index “n” from 2. Thus, this equation is an analytical means to study hardness variation with load. The exponent “n” in the equation is also known as the Meyer index or logarithmic index. Hanemann [16] noticed and concluded that "n" has a value less than 2 in the low load zone, which explains for the increased hardness at low loads. However, Mil’vidskii et al [17] observed the value of “n” in the range from 1.3 to 4.9.

The load dependence of hardness in low load range is thus inevitable. There have been reports of increase of hardness with load in this range. It is also found that the hardness, in any case, reaches a constant value for a range of high loads. Boyarskaya [18] correlated the increase of hardness with load to the penetrated surface layers and the dislocation content in the case of polished and natural faces of NaCl single crystals. In the case of aluminum and magnesium single crystals, Yoshino [19] discovered that the micro hardness grew rapidly with increasing stress, then progressively reduced and eventually became load independent. The decrease in hardness with load is attributed to the heterogeneous deformation and anisotropy.

Single crystals grown by the Bridgman method at a growth speed of 0.35 cm/hr were employed for the microhardness investigation in this work on InSb1-xBix (x=0, 0.03, 0.04, 0.05).

All indentation tests were held on cleavage surfaces of the crystals. The samples were in the form of at least 2 mm thick slices. The indentations were made on freshly cleaved surfaces in all the events. To avoid unwanted anisotropic variations in the measured hardness it is

necessary to keep constant the azimuthal orientation of the indenter with respect to the crystal surface. The first trial indentation was used to orient the diagonal of the indentation mark parallel to this direction. Subsequent indentations were then made keeping this orientation constant. For each measurement, three indentations were made and average diagonal length was used for calculating hardness.

II. VICKERS MICROHARDNESS OF $InSb_{1-x}Bi_x$ (x=0, 0.03, 0.04, 0.05) CRYSTALS:

The Vickers' diamond pyramidal hardness tester was used to make indentations on freshly split surfaces of samples that were at least 2mm thick. Using a micrometre eyepiece, the indentation diagonals were measured to an accuracy of 0.19 μm. The applied stress was varied in the range of 49 mN to 980 mN for the investigation of load dependence of hardness. The hardness was estimated using the Vickers Diamond Pyramidal Indentation's formula:

$$H_v = \frac{1854 \times P}{d^2}$$

where, d is the average of the two indentation mark diagonal lengths in μm, H_v the Vickers hardness in MPa and p is the applied load in mN obtained as the product of the load in gm with g = 9.80 ms^{-2}.

For modest applied loads microhardness is known to have a complex load dependence. The zero-load condition was guaranteed to have a maximum load-error of 1 mN, and a load of 500 mN was chosen to minimise microhardness variations caused by load error. The results are based on an average of at least three indentations created for each variable value and a specific indentation set repeated on two to three samples, as detailed below.

VARIATION OF HARDNESS WITH LOAD:

To eliminate anisotropic variation, the indentations were created with a Vickers pyramidal diamond indenter at different loads ranging from 5 gm to 100 gm for fixed azimuthal orientations of the indenter. The indentation time was kept constant at 30 seconds.

Figures 2, 3, 4 and 5 show the plots of Vickers hardness H_v versus load P, obtained at room temperature, for $InSb_{1-x}Bi_x$ (x=0, 0.03, 0.04, 0.05). The plots indicate clearly that the hardness varies with load in a complex manner. Starting from the smallest load used, the hardness decreases up to a load of about 20 gm. Beyond 20 gm, it reaches saturation.

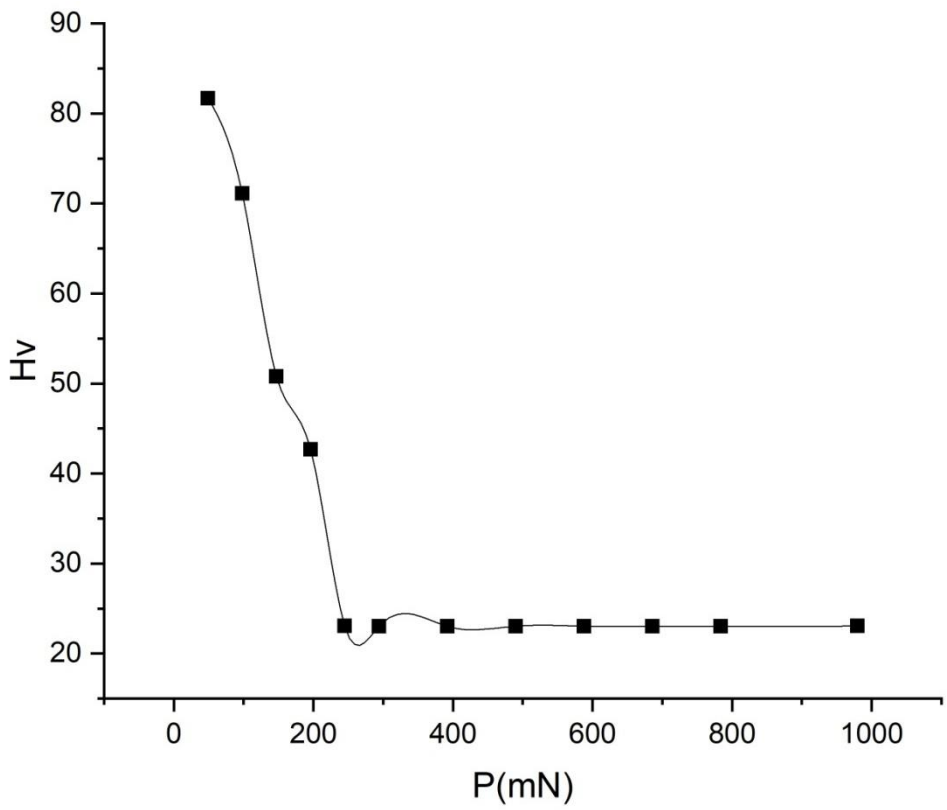

Figure-2 Plot of H_v versus P for InSb crystal

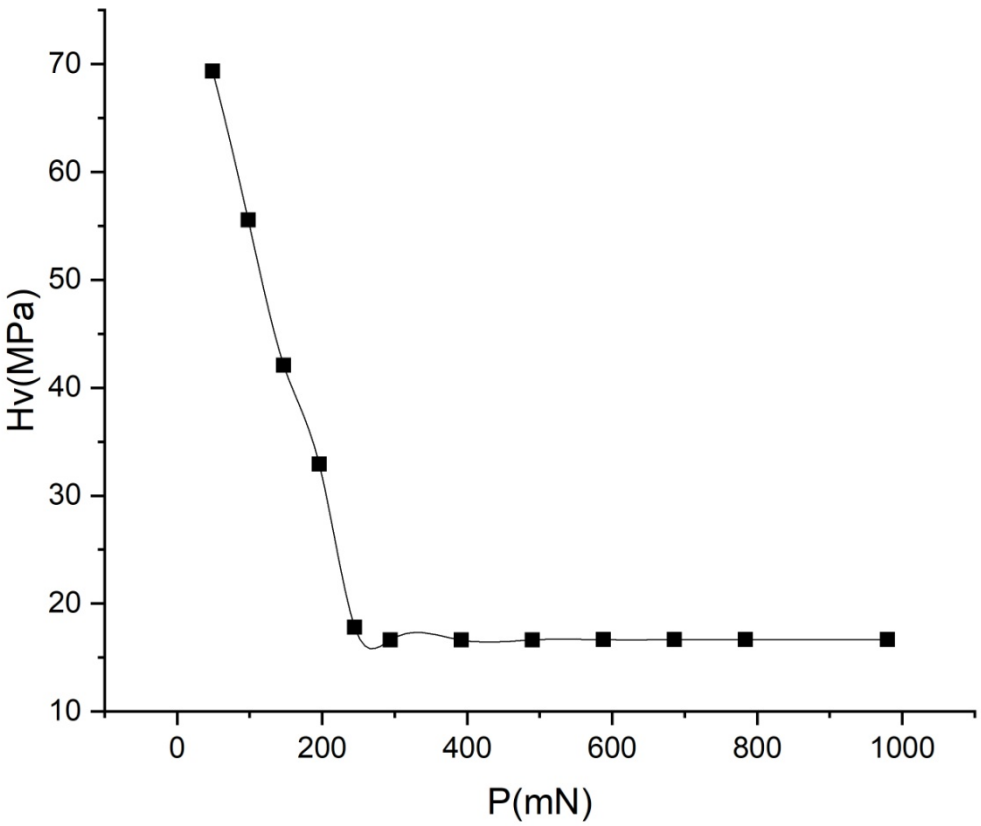

Figure-3 Plot of H_v versus P for $InSb_{0.97}Bi_{0.03}$ crystal

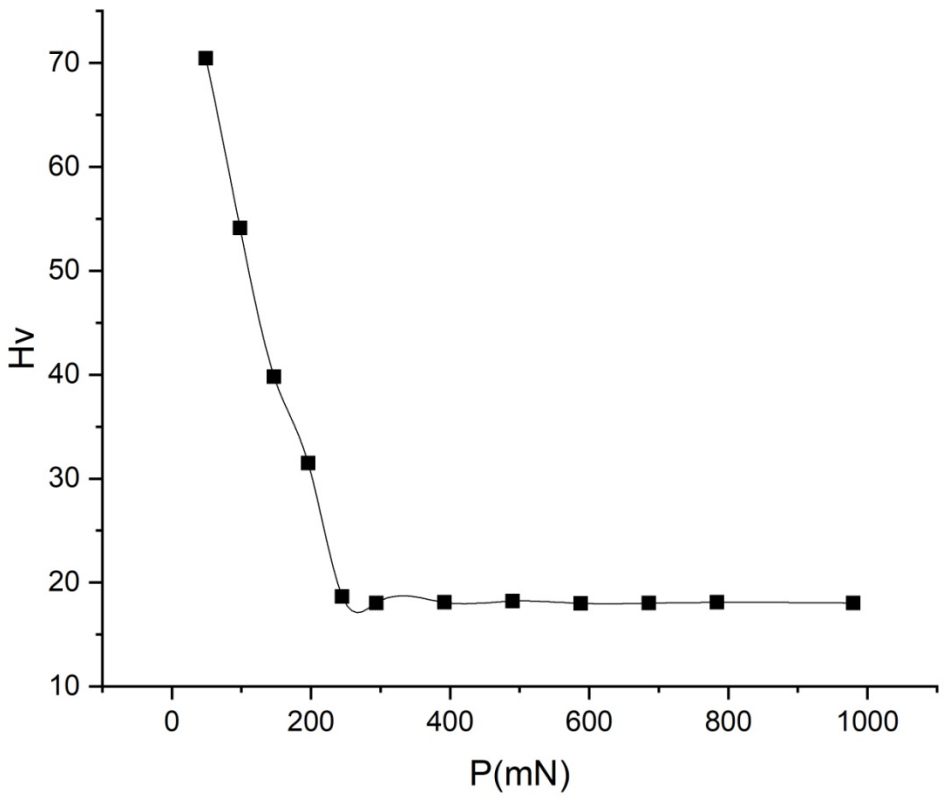

Figure-4 Plot of H_v versus P for $InSb_{0.96}Bi_{0.04}$ crystal

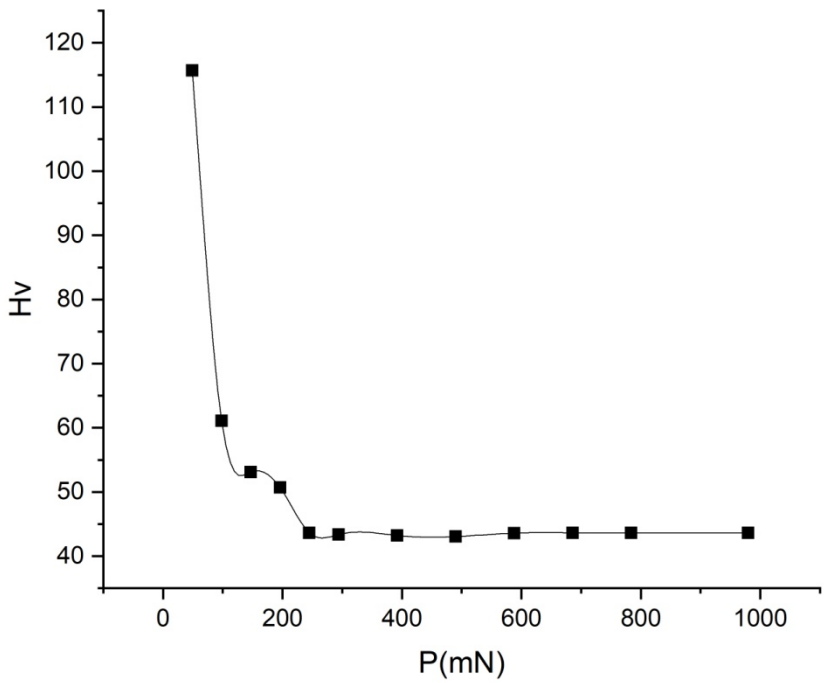

Figure-5 Plot of H_v versus P for $InSb_{0.95}Bi_{0.05}$ crystal

In general, the hardness varies considerably in the low load region as the work hardening capacity and elastic recovery of a particular material are dependent on the load, type of surface receiving the load and the depth to which the surface is penetrated by the indenter. For example, the low load hardness behaviour in the case of silicon single crystal has been explained based on elastic recovery and piling up of material around the indentation mark (Walls et al) [20]. Both the magnitude of work hardening and the depth to which it occurs depends on the properties of the material and are the greatest for soft metallic materials which can be appreciably work hardened. Since the penetration depth at high loads is usually greater than that of the work-hardened surface layer, the hardness value at high loads will be representative of the undeformed bulk of the material and hence independent of load. Even for surfaces that require no mechanical preparation, e.g., cleavage faces of metals and minerals, the hardness obtained at small loads may not still be the same at high loads.

The intricacy seen in the load dependence of hardness is consistent with several observations on other crystals [21-23]. The low load range (i.e., 200 mN or less) defies Kick's Law [24], which states that hardness is independent of load. The strain hardening of the surface layers in response to the loaded indentor's increasing penetration is usually attributed to this dependence [21, 27]. The resulting deformation-induced coherent zones are then used to explain the hardness peaks. The indentor penetrates the virgin layers up to a particular depth of penetration, which corresponds to the thickness of the coherent region and the load at peak hardness. Virgin layers easily favour nucleation and multiplication of dislocations [21, 26]. Beyond 300 mN, the hardness is found to be independent of load and represents the real hardness of the crystal.

Thus, the characteristic hardness values of InSb, $InSb_{0.97}Bi_{0.03}$, $InSb_{0.96}Bi_{0.04}$ and $InSb_{0.95}Bi_{0.05}$ crystals are 2300, 1600, 1800 and 4300 MPa respectively. These values are consistent with the values reported by the authors in the case of the pure InSb, $InSb_{0.96}Bi_{0.04}$ and $InSb_{0.96}Bi_{0.05}$ crystals, *viz*., 2255, 1863 and 4360 MPa, respectively [21,25]. Now the depth of penetration depends usually on three factors:

[1] The type of surface receiving the load can again be divided into three categories:

- Surface layers having different degrees of cold working (Onitsch) [28]

- The surface layer having finely precipitated particles (Buckle) [29] and
- The surface layer has a different grain size (Bochvar et al) [30] and number of grains indented (Onitsch) [31] if the specimen is polycrystalline.

[2] The magnitude of the applied load and

[3] Accuracy in the normal operation of indenting the specimen and the rate at which the indentation is carried out, i.e., the strain rate. The time taken to realize the full load will decide the strain rate.

All these factors play a prominent role when hardness tests are carried out by indentation at low loads. Based on the depth of penetration of the indenter the observed variation of hardness with load in the plot of H_v versus P may be explained. At small loads, the indenter pierces only surface layers and hence the effect is more prominent at those loads. The effect provided by the surface layers of the crystal becomes less pronounced as the depth of penetration increases with load, making the fluctuation of micro hardness with load less evident at higher applied stresses. After a given depth of penetration, the effect of the interior layers becomes increasingly more significant than that of the surface layers and the hardness value with the load is almost unchanged.

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III. MEYER'S INDEX:

In the study of the inter relationship of hardness and load, the Meyer's law is very useful. The law is

$$P = a\, d^n$$

where, n is known as the Mayer index, P = applied load, d = indentation diagonal length, a = material constant. The load-dependent hardness is reflected in the deviation of the value of n from 2 [32]. This law can be written as

$$\ln P = \ln a + n \ln d$$

Based on the d and p data, graphs of ln P versus ln d were obtained. This is shown in figure 6, 7, 8 and 9 (x = 0, 0.03, 0.04, 0.05) for $InSb_{1-x}Bi_x$ crystals.

The graph of ln p in against ln d (where d = the length of the through diagonal) follows Meyer's law [33]. In different load ranges, $p = a\, d^n$ has different values (figure 7-10). In the high load range, it is observed to be near to 2, indicating that hardness saturation has occurred in this load range.

Nonlinearity at low loads appears to be significantly affected by an unpredictable load relationship, but as the graph shows, it does not follow a linear relationship.

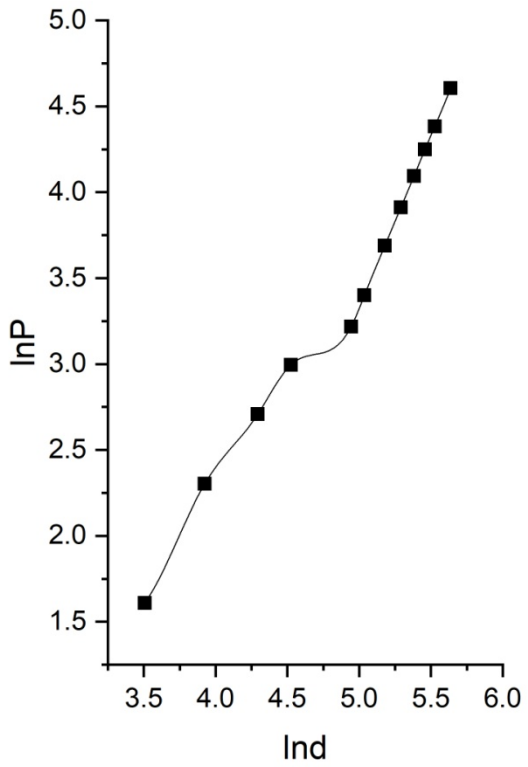

Figure-6 Plot of lnP versus lnd for InSb crystal

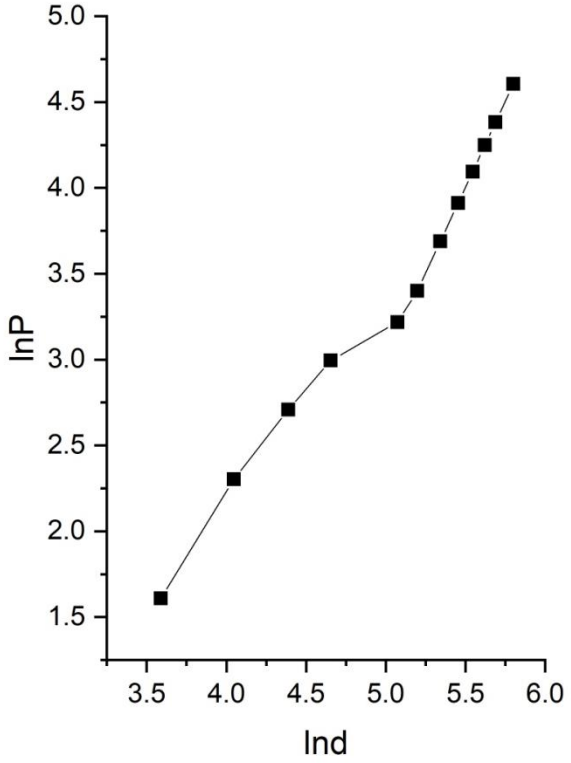

Figure-7 Plot of lnP versus lnd for $InSb_{0.97}Bi_{0.03}$ crystal

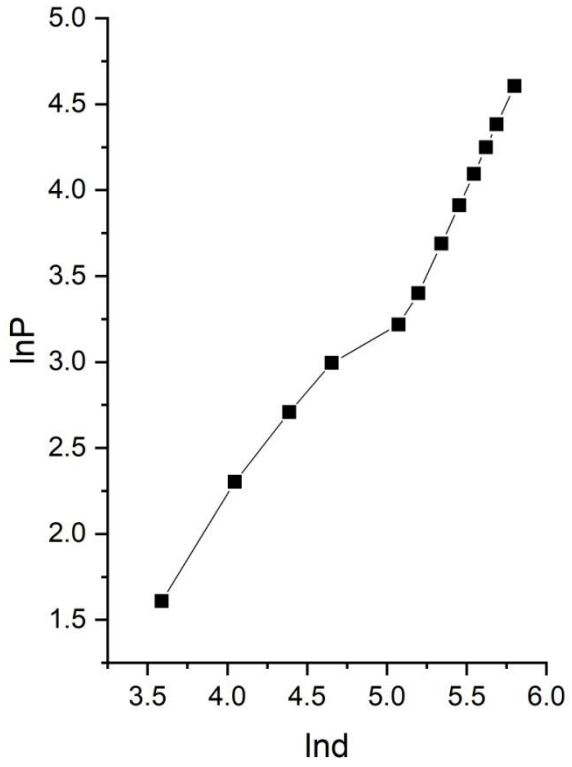

Figure-8 Plot of lnP versus lnd for $InSb_{0.96}Bi_{0.04}$ crystal

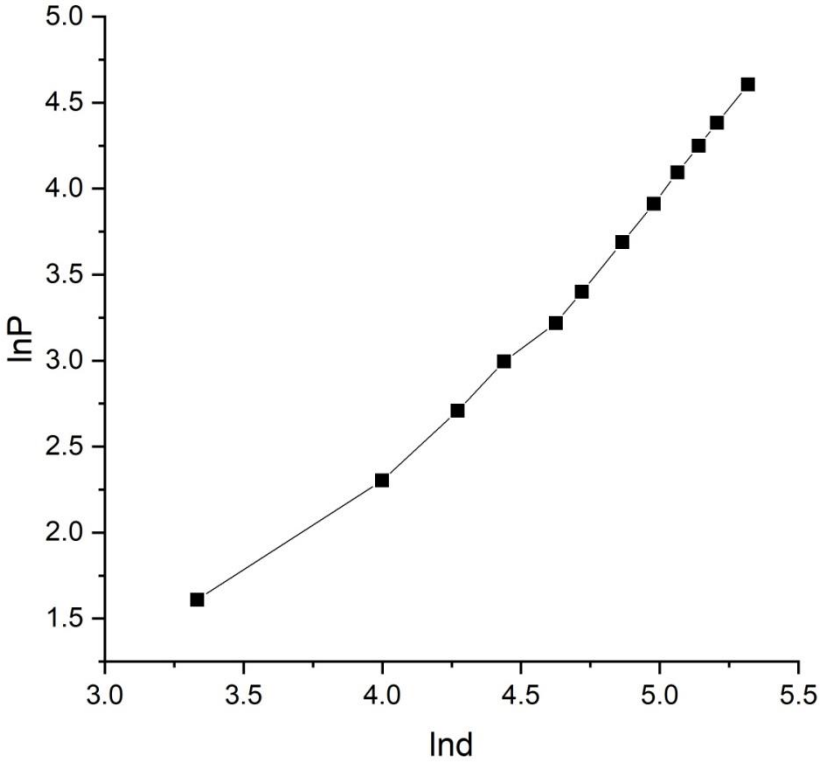

Figure-9 Plot of lnP versus lnd for $InSb_{0.95}Bi_{0.05}$ crystal

IV. Conclusions:

1. The hardness values of InSb, $InSb_{0.97}Bi_{0.03}$, $InSb_{0.96}Bi_{0.04}$ and $InSb_{0.95}Bi_{0.05}$ crystals are 2300, 1600, 1800 and 4300 MPa respectively.
2. Micro hardness is a load-dependent property with significant variation in low load ranges, becoming virtually load independent only for sufficiently large applied stresses.
3. The hardness peaks observed in H_v versus load (P) plots may be explained in terms of deformation-induced coherent regions.
4. Due to work hardening, the crystal hardness increases. The Mayer index is not truly constant but may be different in different load ranges.

References:

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