# CHAPTER – 7

## MICROHARDNESS OF $Bi_{1-X}Sb_X$ SINGLE CRYSTALS

The results of microharness studies on $Bi_{1-x}Sb_x$ ( x= 0.05,0.10,0.15,0.20,0.25,0.30) are presented in this chapter. Microhardness indentation tests were carried out on the cleavage planes (111) of the $Bi_{1-x}Sb_x$ crystals by using the Vickers diamond pyramidal indenter and Knoop indenter. The applied load dependence of hardnes has also been studied.

## INTRODUCTION:

The indentation method is the most widely used method for measurement of hardness of the crystals either of metallic or nonmetallic nature. This method does not require large specimens and even on a small specimen a number of measurements can be carried out. Among the various factors on which the measured value of hardness depends, friction and prior strain hardening also depends on the geometry of the indenter. The indenter used must be either sharp or blunt according to their included angles which are less or greater than $90^0$. As this angle increases, the indenter tends to be blunt and influence of friction and prior strain hardening decreases. Also, the value of the constraint factor "C" in the relation between hardness and yield stress (H = CY), tends to 3 as the 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 $136^0$ which is a good compromise to minimize frictional effects and at the same time to give a well defined geometrically shaped indentation mark. The geometry of the indenter is shown below:

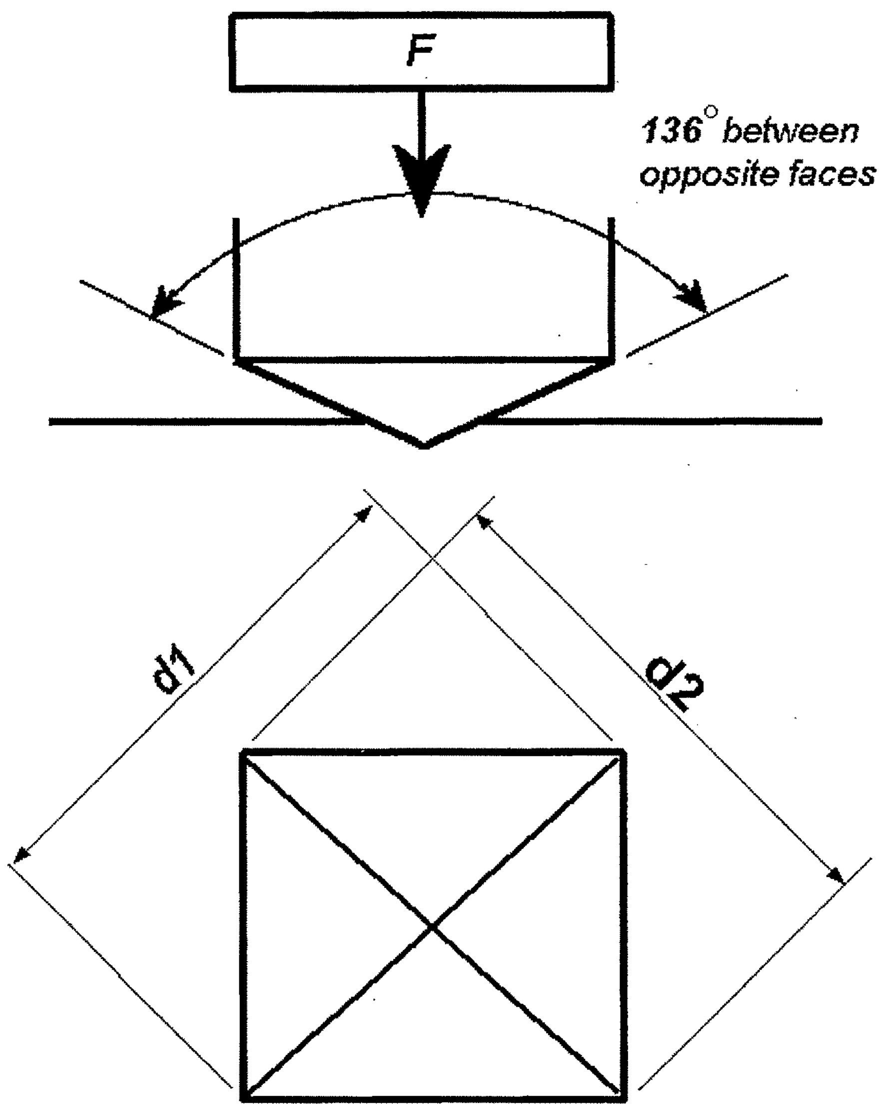


**Figure -1** Vicker's indentor

Also during the diamond contact with the cleavage surface of a metal, the coefficient of friction ranges from 0.1 to 0.15 making the frictional effects less pronounced (Tabor)[2]. The Vickers hardness is defined as the ratio of applied load to the pyramidal contact area of indentation and it is calculated as

$$H_v = \frac{1854 \times 9.8 \times P}{d^2} \quad \text{Mpa} \quad \ldots\ldots.. (1)$$

where,

$H_v$ = Vickers microhardness 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 imply the hardness to be independent of load. However, this is not the case and except for loads exceeding about 200 gm (i.e. 1960 mN) in general, the measured hardness value has been found to depend on load in almost all cases and hence the hardness values measured in the low load region (< 200gm. i.e., < 1960 mN), are known as micro hardness values. Though, the limit load is not sharply defined and practically the hardness may achieve a constant value for loads in the range 20 to 50 gm (i.e., 196 to 490 mN) and beyond, depending on the material.

In general, the nature of variation of hardness with load is quite complex and does not follow any universal rule. Many workers have studied the load dependence of hardness and the results obtained are quite confusing. As for example, Bergsman observed a very pronounced load dependence of hardness[3]. The load variation of hardness was studied by Rostoker[4] in the case of copper and observed a decrease in hardness at low applied loads. In contrast to this, a considerable increase in the hardness values at low applied loads was observed by Buckle[7]. This increase in the hardness value has been observed due to elastic recovery after removing the applied load which reduces the diagonal length. For sintered carbides, Grodzinsky[8] found that the plot of hardness versus load shows a peak at low applied loads. Knoop et al[9] and Bernhadt[11] found the increase in the hardness value with decreasing load. On the other hand, Campbell et al[5] and Mott et al[10] observed a decrease in hardness with decrease in load. Whereas, Taylor[6] and Toman et al[12] have reported no significant change in the hardness value with variation of load. Such contradictory results[5-13] may be due to the effects of the surface layers and vibrations produced during the work. Gane et al[14] studied the microhardness at very small loads. They observed a sharp increase in hardness at small indentation sizes and suggested that this increase may be due to the high stresses required for homogeneous nucleation of dislocations in the small dislocation free regions indented. On the contrary, Ivan'ko[15] found a microhardness decrease with decreasing load and concluded that this dependence is due to the relative contributions of plastic and elastic deformations in the indentation process.

According to these different observations and reports, it can be said that it is difficult to establish any definite relationship between microhardness and applied load. As shown in equation 1, the hardness, to be independent of load P, should be directly proportional to the square of the diagonal length "d". Thus,

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

Where "a" is a material constant. This equation is known as Kick's law. According to the above discussion, the observed hardness dependence on load implies that the power index in this equation should differ from 2 and according to Hanemann[16], the general from of dependence of load on the diagonal length should be in the form of

$$P = ad^n \;\ldots\ldots\;\ldots\ldots\;\ldots\ldots \qquad (3)$$

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 Meyer index or logarithmic index. Hanemann[16] observed and concluded that in the low load region, 'n' generally has a value less than 2, which accounts for the higher 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] observed that the microhardness increased rapidly first with the increasing load and then decreased gradually and finally became independent of load. The decrease in hardness with load is attributed to the heterogeneous deformation and anisotropy.

In the present work on $Bi_{1-x}Sb_x$ ( x=0.05,0.10,0.15,0.20,0.25,0.30) single crystals grown by the zone melting method after 8 zone levelling passes at the growth speed of 1 cm/hr were used for the microhardness study and the results are discussed below.

All indentation tests were carried out on cleavage surfaces of the crystals. The samples were in the form of at least 3 to 4 mm thick slices. The indentations were made on freshly cleaved surfaces in all the cases. 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.

## VICKERS HARDNESS OF $Bi_{1-x}Sb_x$ CRYSTALS :

The indentations were performed at a very slow rate and for all indentations, care was taken to see that the rate was nearly the same. Also, between two neighboring indentation marks on the same surface, a separation of at least three indentations was maintained to avoid interference.

The indentation mark was square in shape. The Diagonals of indentation mark were measured using micrometer eyepiece with least count 0.19 micron.

## VARIATION OF HARDNESS WITH LOAD:

The indentations using Vickers pyramidal diamond indenter were made at different loads ranging from 1 gm to 160 gm for fixed azimuthal orientations of the indenter to avoid anisotropic variation as described earlier. The indentation time was kept constant at 30 second.

Figures 2,3,4,5,6 and 7 show the plots of Vickers hardness $H_v$ versus load P, obtained at room temperature, for $Bi_{1-x}Sb_x$ (where x = 0.05,0.1,0.15, 0.20,0.25, 0.3). The plots indicate clearly that the hardness varies with load in a complex manner. Starting from smallest load used, the hardness increases up to a load of about 50 gm. Beyond 50 gm, it reaches saturation.

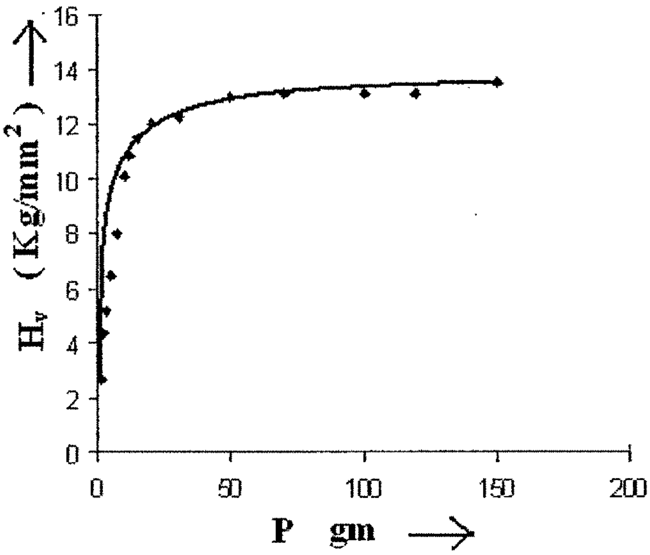


**Figure –2** $Bi_{0.95}Sb_{0.05}$

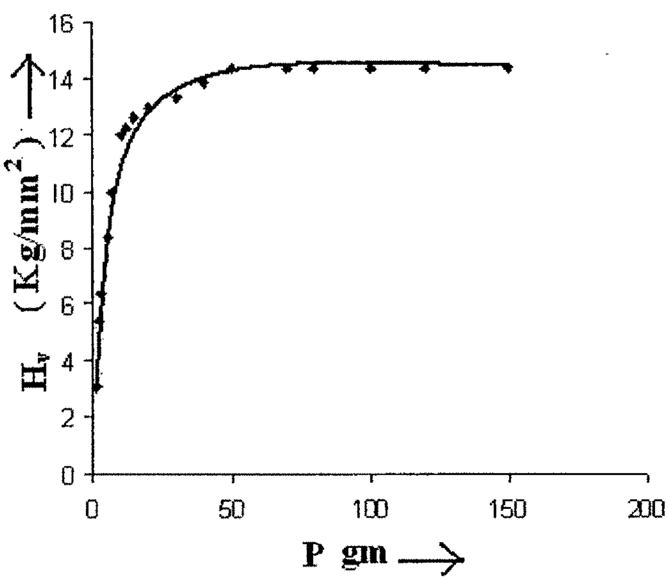


**Figure –3** $Bi_{0.90}Sb_{0.10}$

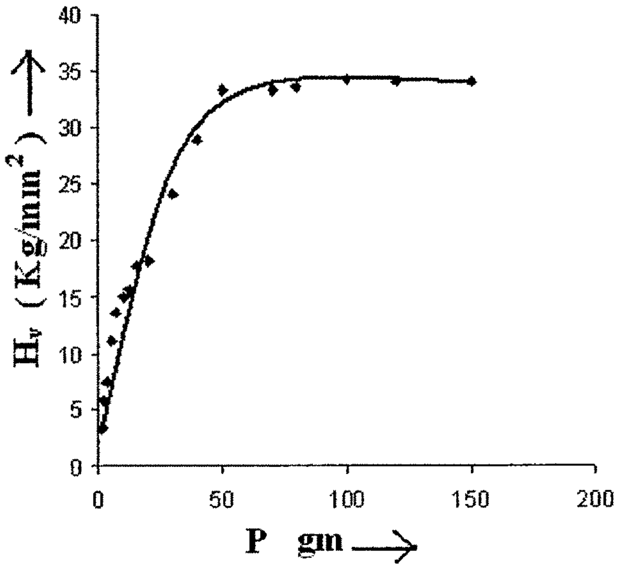


Figure –4 $Bi_{0.85}Sb_{0.15}$

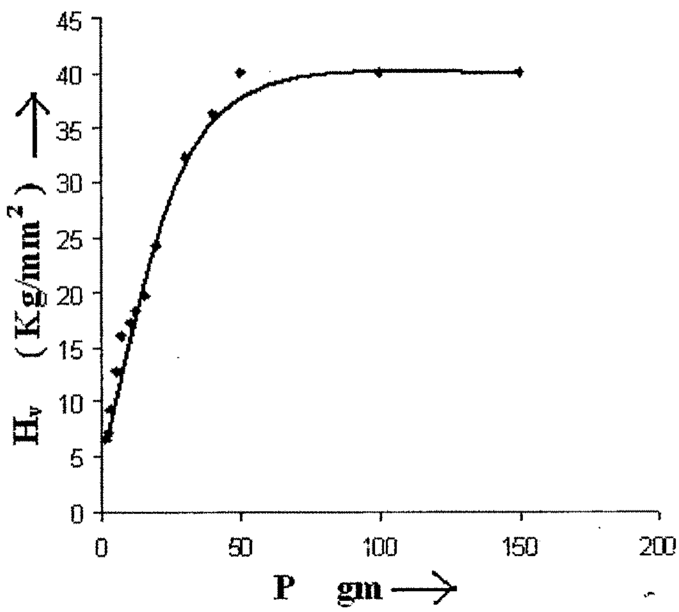


Figure –5 $Bi_{0.80}Sb_{0.20}$

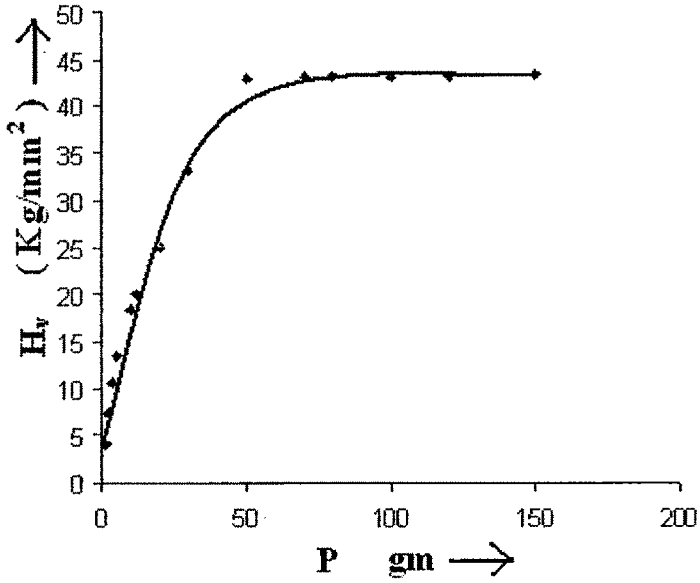


**Figure –6** **$Bi_{0.75}Sb_{0.25}$**

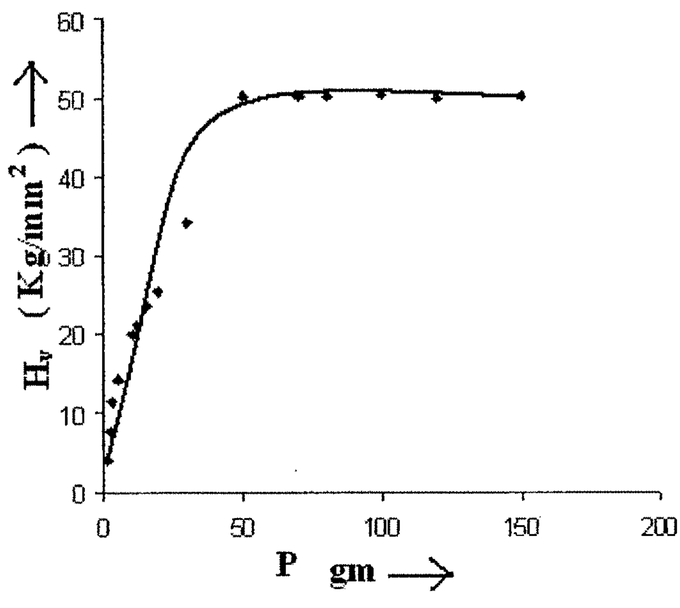


**Figure –7** **$Bi_{0.70}Sb_{0.30}$**

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 behavior in the case of silicon single crystal has been explained on the basis of 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 depend 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 unreformed bulk of the material and hence independent of load. Even for surfaces which 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.

Now the depth of penetration depends usually on three factors:

[1].The type of surface receiving the load which can again be divided in to three categories :

→ Surface layers having different degrees of cold working (Onitsch)[21]

→Surface layer having finely precipitated particles (Buckle)[22] and

→ Surface layer having different grain size (Bochvar et al)[23] and number of grains indented (Onitsch)[24], if the specimen is a polycrystal.

[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 evidently decide the strain rate.

All these factors play a prominent role when hardness tests are carried out by indentation at low loads. On the basis of depth of penetration of the indenter the observed variation of hardness with load in the plot of $H_v$ v/s P may be explained. At small loads, the indenter pierces only surface layers and hence the effect is more prominent at those loads. As the depth of penetration increases with load, the effect posed by the surface layers of the crystal becomes less sharp which makes the variation of microhardness with load less prominent at higher applied loads. After certain depth of penetration, the effect of inner layers becomes more and more prominent than those of the surface layers and ultimately there is practically no change in the hardness value with load.

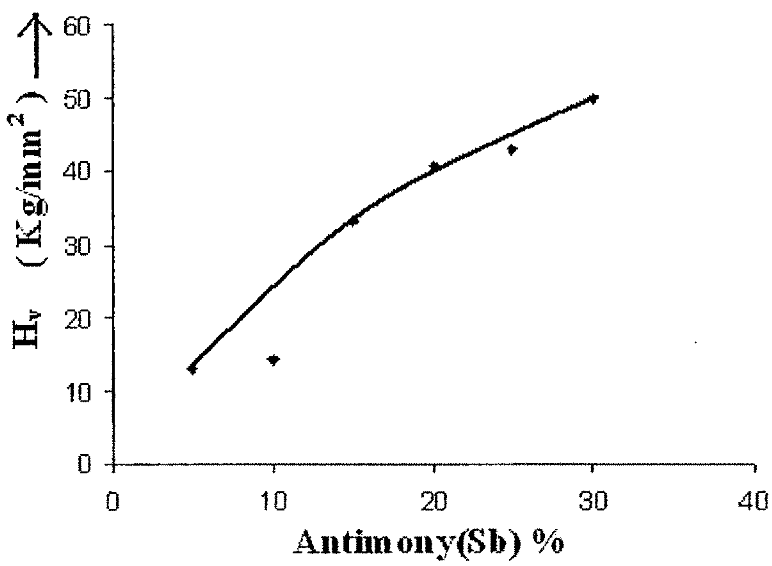


**Figure- 8 Vicker's Hardness→ Sb%**

Thus, the bulk characteristic hardness is usually represented by the value in the saturation region. The results in the present case can be summarized as in Table-1 which lists the constant hardness values obtained from these plots for crystals with different Sb concentrations. The hardness obtained from these data is plotted in figure.8 as a function of Sb concentration. The hardness increases with increase in the concentration of Antimony( Sb) as can be expected on the basis of impurity hardening phenomenon.

## MEYER'S INDEX :

The Meyer's law is also useful in analyzing dependence of hardness on load. The law is

$$P=ad^n ,$$

where the index n is known as Meyer's index, and P =applied load and d= diagonal length of the indention mark, where as, a= material constant. Load dependence hardness is reflected in the deviation of the value of n from 2 reflects[25]. This law can be written as

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

From the data of d and p, the plots of ln p Vs ln d were obtained. These plots are shown in Fig 9,10,11,12,13 and 14 for $Bi_{1-x}Sb_x$ ( x= 0.05,0.10,0.15,0.20,0.25,0.30 ) crystals, respectively. The slope of the graph gives the value of Meyer's index.

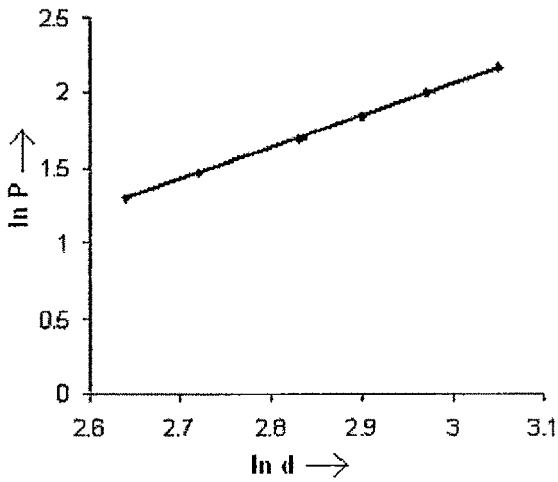


**Figure -9** $Bi_{0.95}Sb_{0.05}$

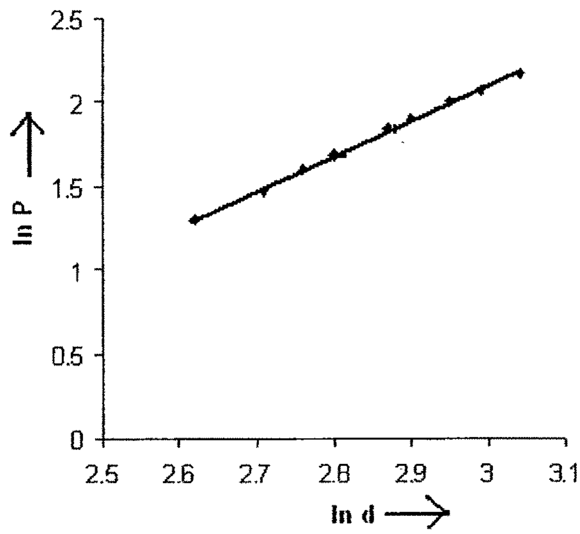


**Figure -10** $Bi_{0.90}Sb_{0.10}$

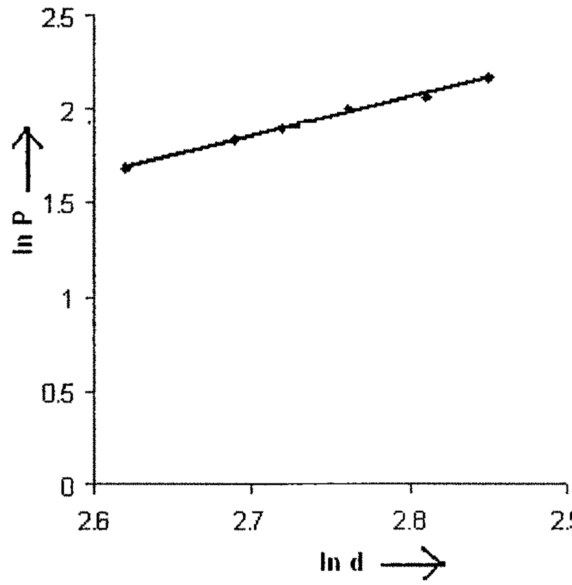


**Figure -11** $Bi_{0.85}Sb_{0.15}$

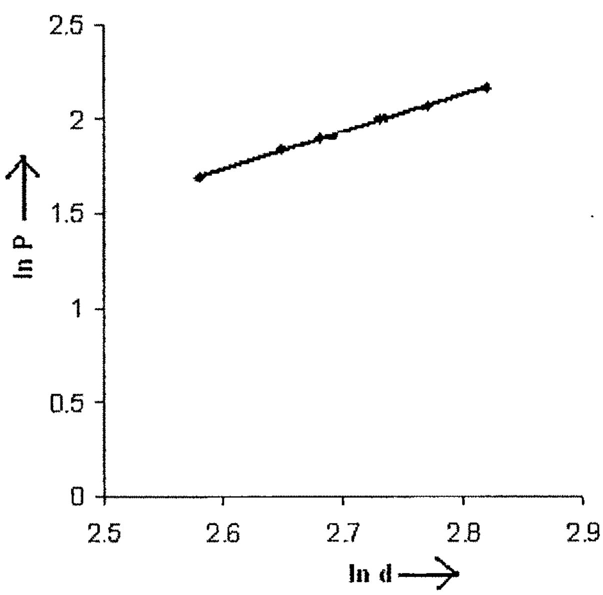


**Figure -12** $Bi_{0.80}Sb_{0.20}$

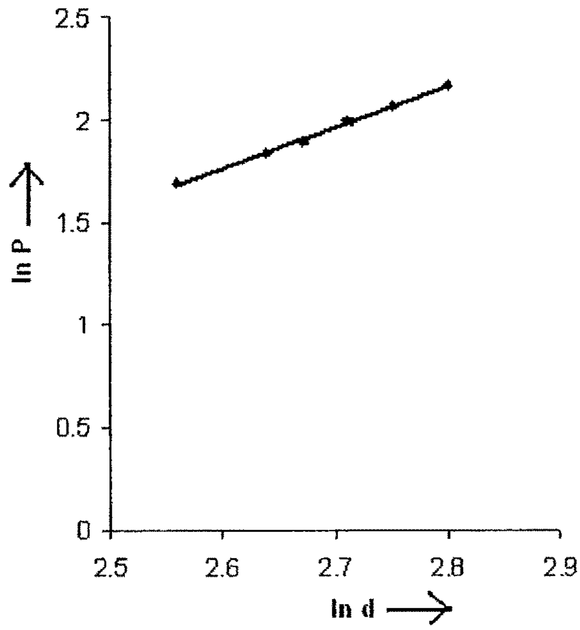


**Figure -13** $Bi_{0.75}Sb_{0.25}$

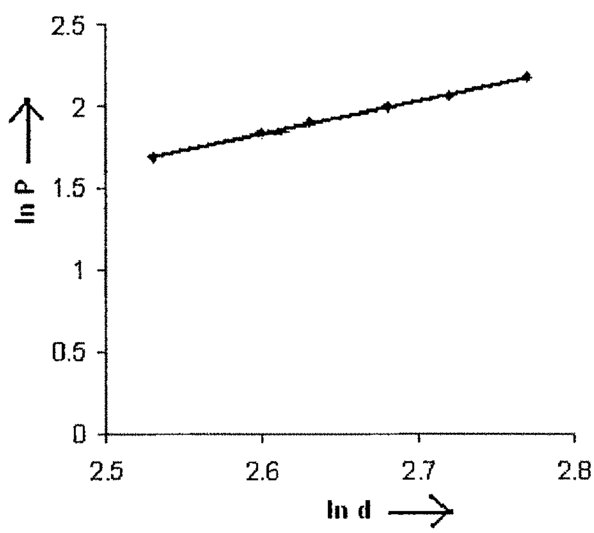


**Figure -14** $Bi_{0.70}Sb_{0.30}$

The values of Vicker's hardness and Meyer index obtained in the present case are given in table-1

**Table - 1**

| Material | Hardness ( $Kg/mm^2$) | Meyer Index |
|---|---|---|
| $Bi_{0.95}Sb_{0.05}$ | 13.00 | 2.11 |
| $Bi_{0.90}Sb_{0.10}$ | 14.00 | 2.09 |
| $Bi_{0.85}Sb_{0.15}$ | 33.22 | 2.05 |
| $Bi_{0.80}Sb_{0.20}$ | 40.65 | 1.98 |
| $Bi_{0.75}Sb_{0.25}$ | 43.00 | 2.02 |
| $Bi_{0.70}Sb_{0.30}$ | 50.13 | 1.98 |

## KNOOP HARDNESS STUDY OF $Bi_{1-x}Sb_x$ CRYSTALS :

The Knoop indenter is also a diamond indenter like the Vicker's indenter. The geometry of the Knoop indenter is shown in figure 15. The Knoop hardness indenter is specially suitable to study the surface anisotropy in hardness. However, the hardness variation with load is the concern of the present study. The shape of indenter is such that it gives elongated rhombus shape of the indentation mark with one of the two diagonals quite longer, about seven times than the other[26]. The value of Knoop hardness is given by,

$$H_k = 14230\ P/d^2$$

where, P= load in gm and d = longer diagonal length in microns.

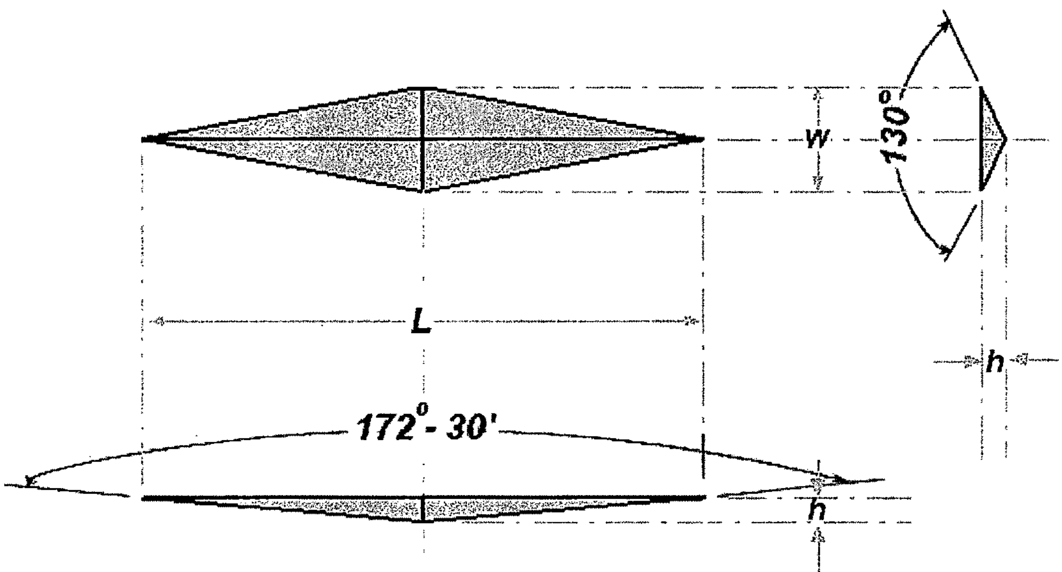


Figure 15 Knoop indenter

The Knoop hardness variation with load, for $Bi_{1-x}Sb_x$ (x=0.05 to 0.30) is shown in figures 16-21, respectively.

The plots indicate clearly that the hardness varies with load in a complex manner. Increase in hardness at low load values is a common feature observed in all the plots. The hardness reaches a peak and displays complex variation with increase in load and becomes constant at sufficiently high loads as can be seen from the plots. The decreasing trend before saturation is a new feature here not observed in the case of Vickers hardness. The hardness obtained from these data is plotted in figure 22.The load dependence analysis based on Meyer's law has been shown in term of plot of ln P→ ln d in figures 23-28 for $Bi_{1-x}Sb_x$ (x=0.05 to 0.30). The Meyer index and the hardness values ( saturation region) are tabulated in Table-2. The $H_k$ values fairly agree with the previous report [27]. Here also the hardness increases with x while the Meyer index nearly follows the behavior observed in the case of Vicker's hardness. Significantly, it is observed that the Knoop hadness values of these alloys are larger than their Vickers hardness value.

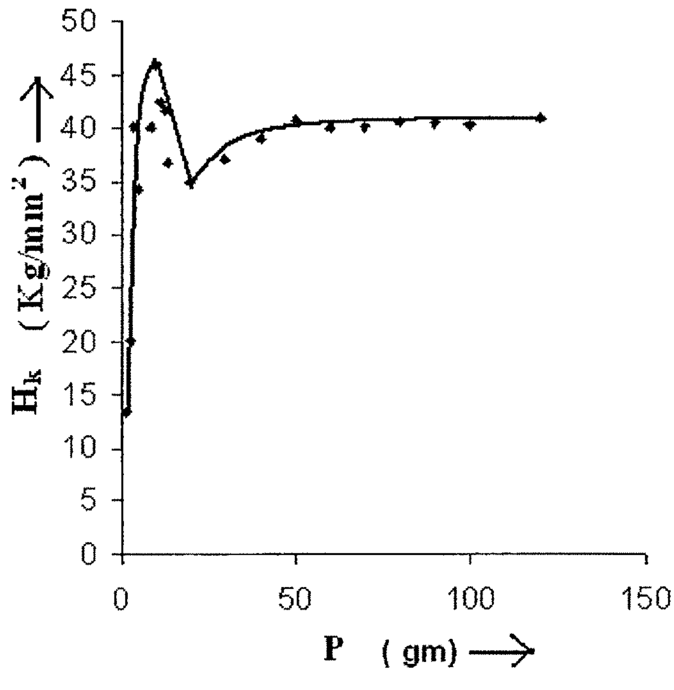


Figure-16 $Bi_{0.95}Sb_{0.05}$

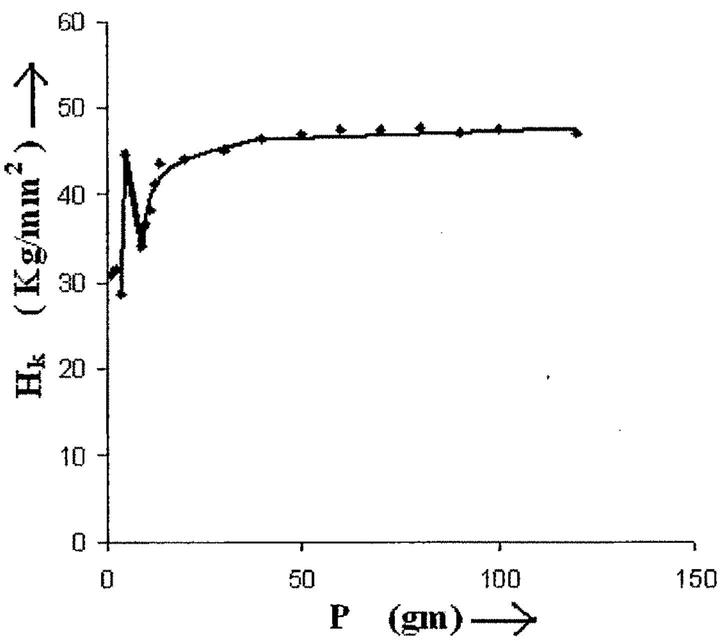


Figure- 17 $Bi_{0.90}Sb_{0.10}$

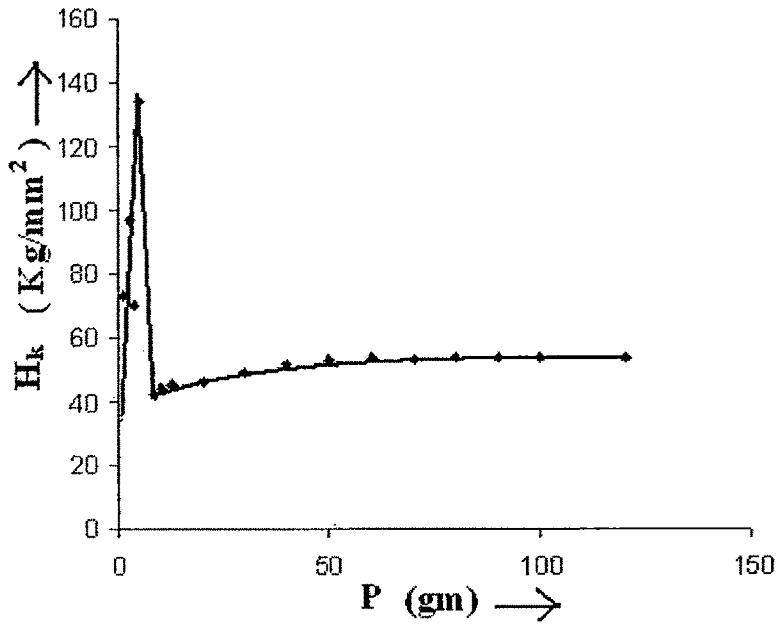


Figure- 18 $Bi_{0.85}Sb_{0.15}$

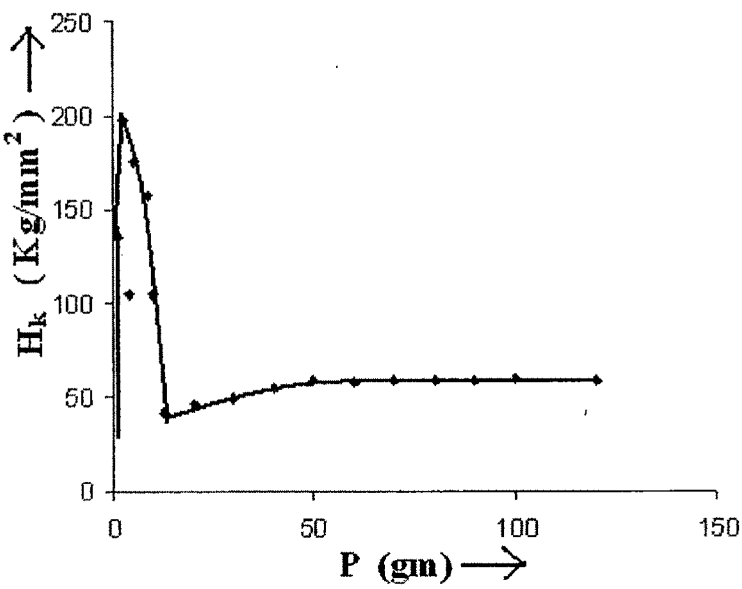


Figure- 19 $Bi_{0.80}Sb_{0.20}$

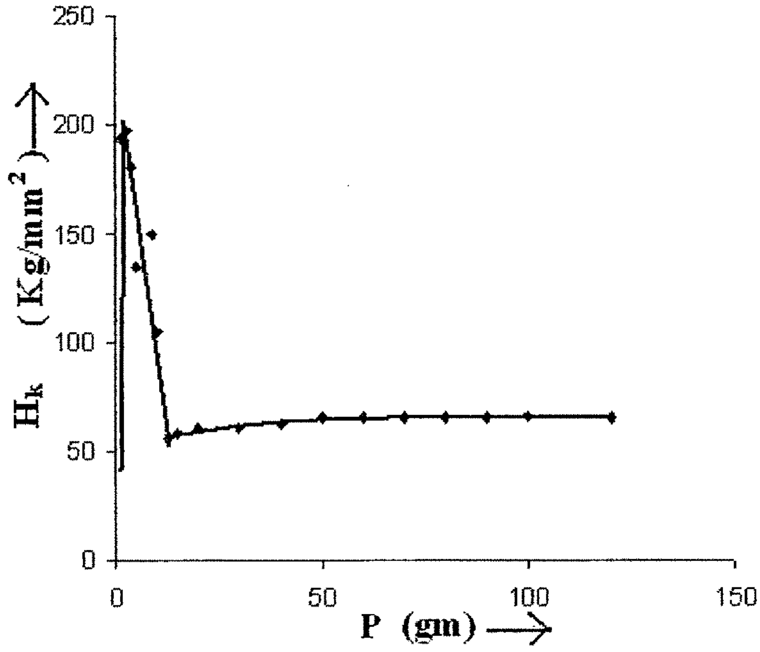


Figure-20 $Bi_{0.75}Sb_{0.25}$

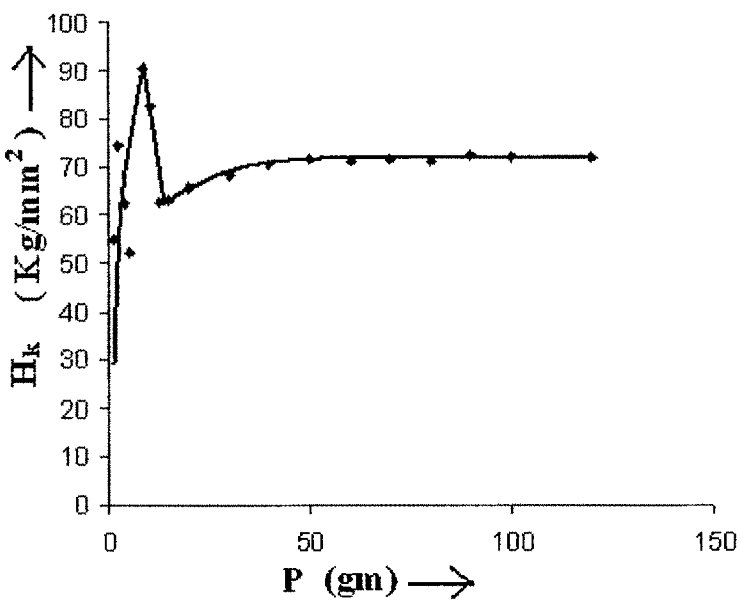


Figure-21 $Bi_{0.70}Sb_{0.30}$

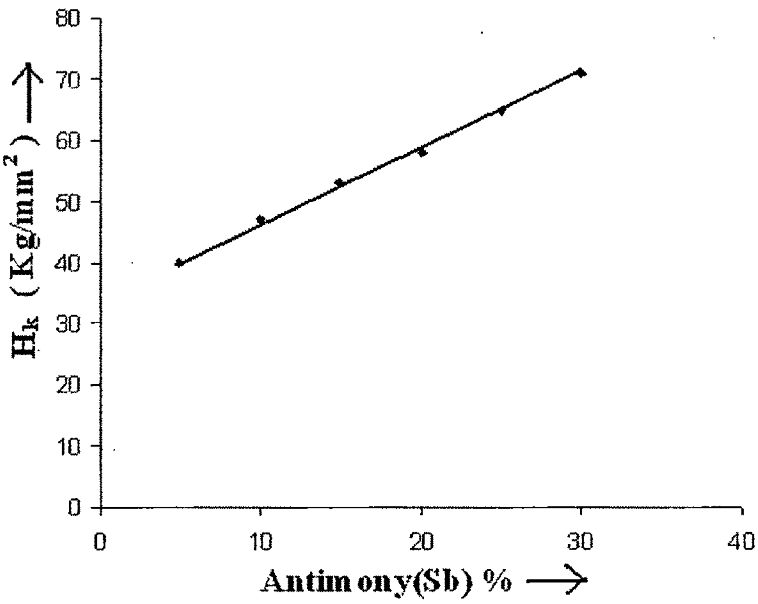


Figure-22

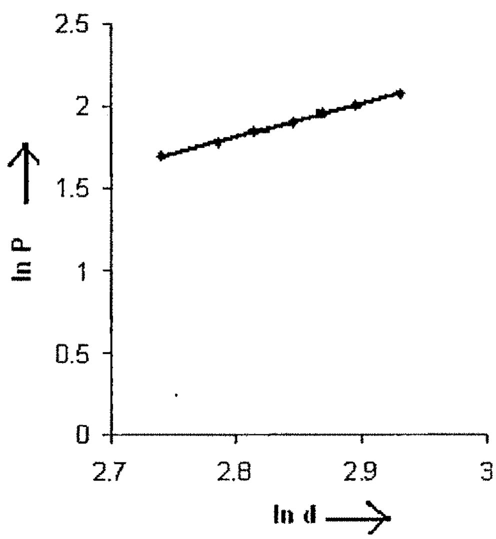


Figure-23 $Bi_{0.95}Sb_{0.05}$

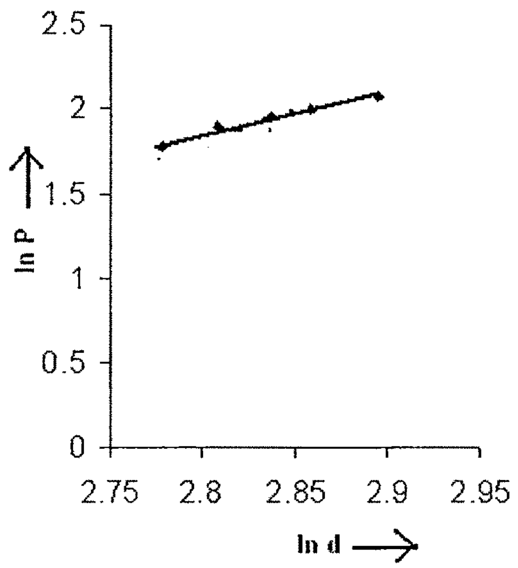


**Figure-24** $Bi_{0.90}Sb_{0.10}$

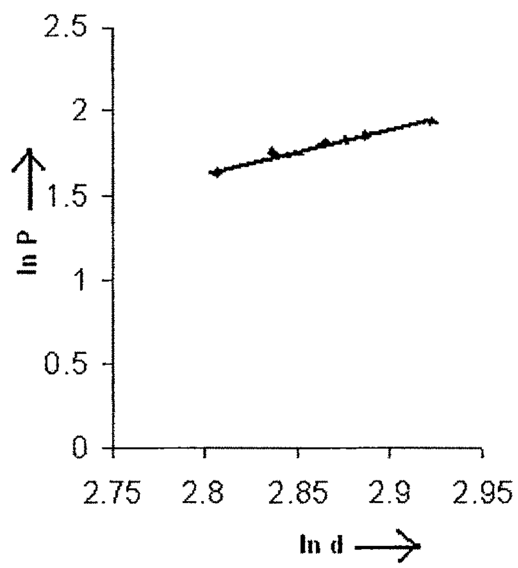


**Figure-25** $Bi_{0.85}Sb_{0.15}$

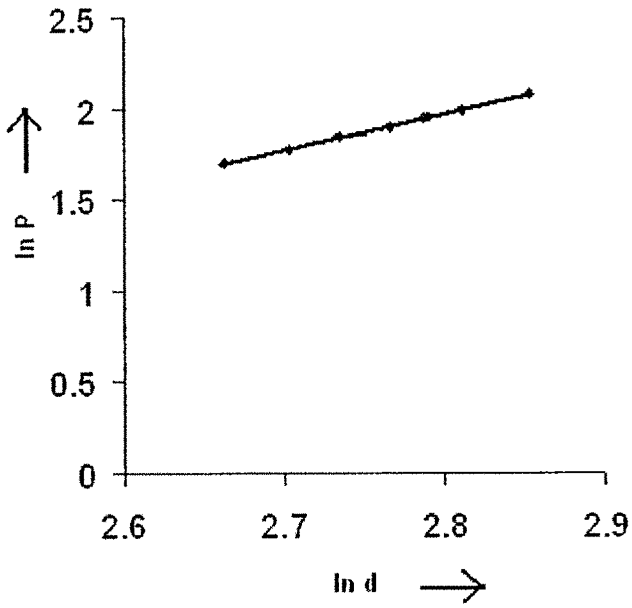


**Figure 26** $Bi_{0.80}Sb_{0.20}$

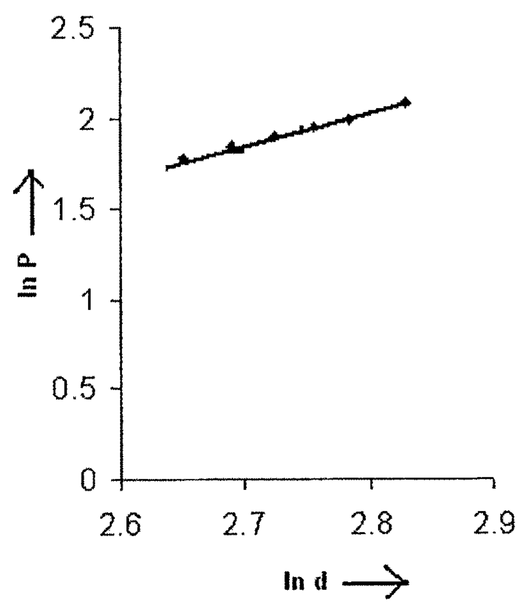


**Figure 27** $Bi_{0.75}Sb_{0.25}$

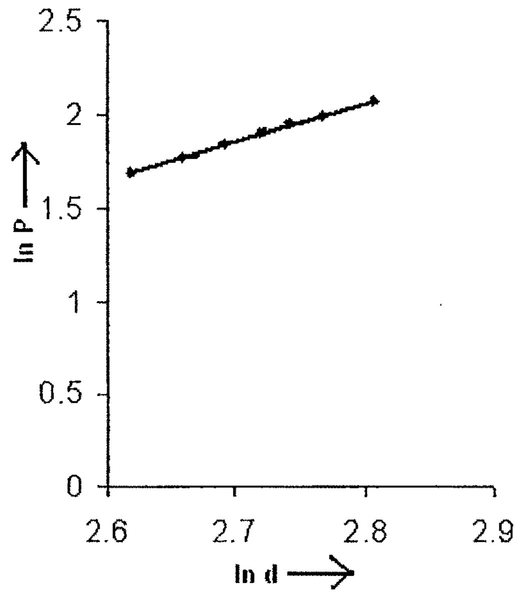


**Figure 28** $Bi_{0.70}Sb_{0.30}$

**TABLE - 2**

| Material | Knoop Hardness( $Kg/mm^2$) | Meyer Index |
|---|---|---|
| $Bi_{0.95}Sb_{0.05}$ | 40.14 | 2.00 |
| $Bi_{0.90}Sb_{0.10}$ | 47.32 | 2.03 |
| $Bi_{0.85}Sb_{0.15}$ | 53.22 | 2.01 |
| $Bi_{0.80}Sb_{0.20}$ | 58.65 | 2.02 |
| $Bi_{0.75}Sb_{0.25}$ | 65.18 | 1.86 |
| $Bi_{0.70}Sb_{0.30}$ | 71.17 | 2.02 |

## CONCLUSIONS:

- Hardness of $Bi_{1-x}Sb_x$ increases with x, in both the cases.( Vicker's hardness and Knoop hardness )

- Hardness is dependent on load in the low load range.

- The Meyer index analysis indicates the load dependent nature of hardness of both Vicker's hardness and Knoop hardness of $Bi_{1-x}Sb_x$ crystals.

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