CHAPTER 4

MICRO HARDNESS OF $Bi_{2-x}Sb_xTe_3$(x=0, 0.05, 0.1, 0.2) SINGLE CRYSTALS

The indentation method is the most widely used methods for measurement of hardness of the crystals either of metallic or nonmetallic nature, and by this method on a small specimen a number of measurements can be carried out. This is the major advantage of this method. There are among the various factors on which the measured value of hardness depend, friction and prior strain hardening also depends on the geometry of the indenter, it is either sharp or blunt consistent with their angles which are less or bigger than 90º. 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:

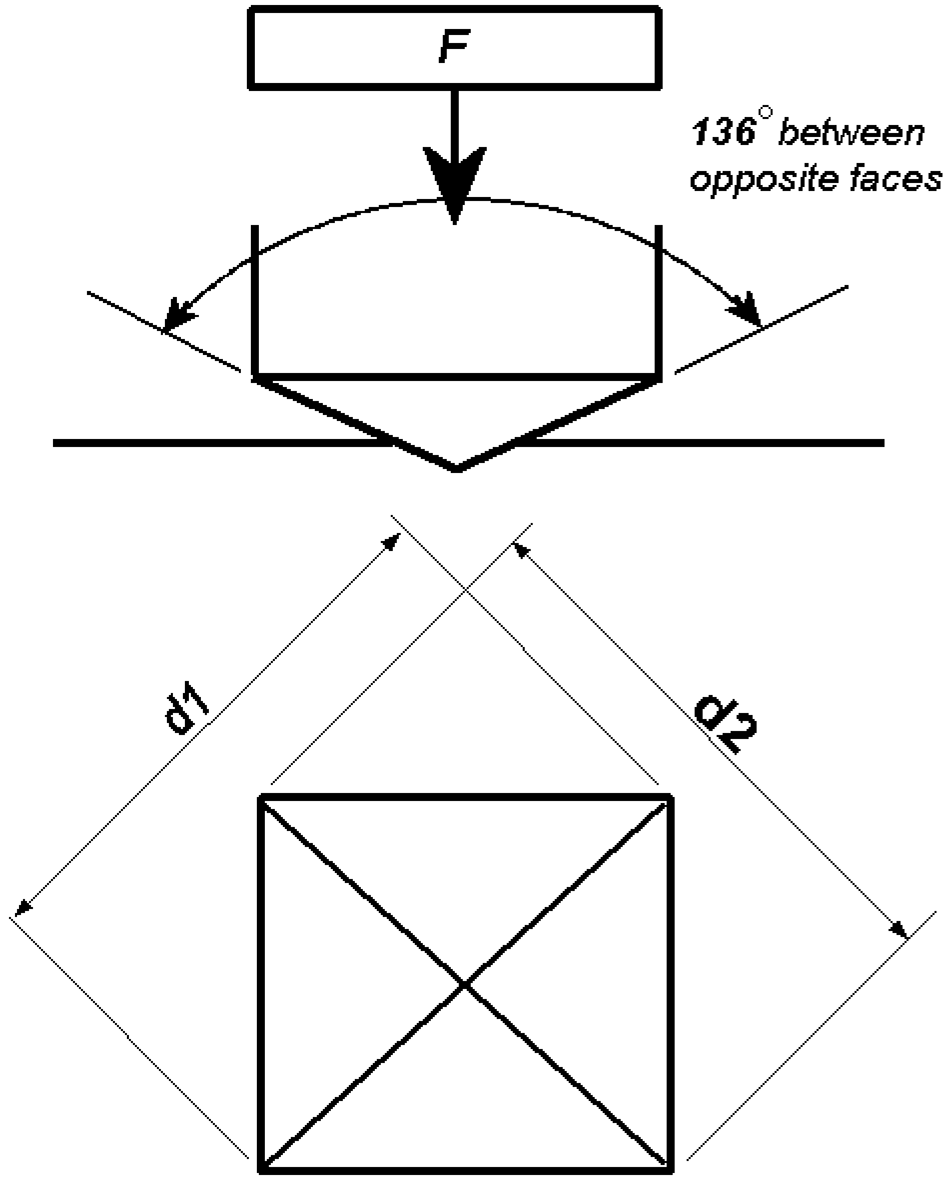

Figure -1 Vickers indentor

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

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

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 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 [9]. 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[11] found that the plot of hardness versus load shows a peak at low applied loads. Knoop et al [5] and Bernhadt[6] found the increase in the hardness value with decreasing load. On the other hand, Campbell et al [7] and Mott et al [10] observed a decrease in hardness with decrease in load. Whereas, Taylor [8] 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,

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

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

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

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 $Bi_{2-x}Sb_xTe_3$(x=0,0.05,0.1,0.2) single crystals grown by the Bridgman method at the growth speed of 0.35 cm/hr were used for the microhardness study and the results are discussed below.

All indentation tests were held out 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.

VICKERS MICROHARDNESS OF $Bi_{2-x}Sb_xTe_3$(x=0,0.05,0.1,0.2)CRYSTALS :

The hardness indentations were carried out on freshly cleaved surfaces of samples of at least 2mm thick, using Vickers diamond pyramidal hardness tester. The indentation diagonals were measured to an accuracy of 0.19 μm using a micrometer eye piece. For the study of load dependence of hardness, the applied load was varied in the range from 10 mN to 1000 mN. The hardness was calculated using the formula appropriate for the Vickers Diamond Pyramidal Indentation:

$$H_v = \frac{1854p}{d^2}$$

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

It is known that microhardness has complex load dependence for small applied loads. The zero load condition was assured to give a maximum load-error to be 1 mN and a load of 500 mN was selected to minimize microhardness variations due to error in applied load. The results, discussed below, are based on the observations averaged over at least three indentations produced at each variable value and a particular indentation set repeated on two to three samples.

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 and 5 show the plots of Vickers hardness H_v versus load P, obtained at room temperature, for $Bi_{2-x}Sb_xTe_3$(x=0,0.05,0.1,0.2). 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.

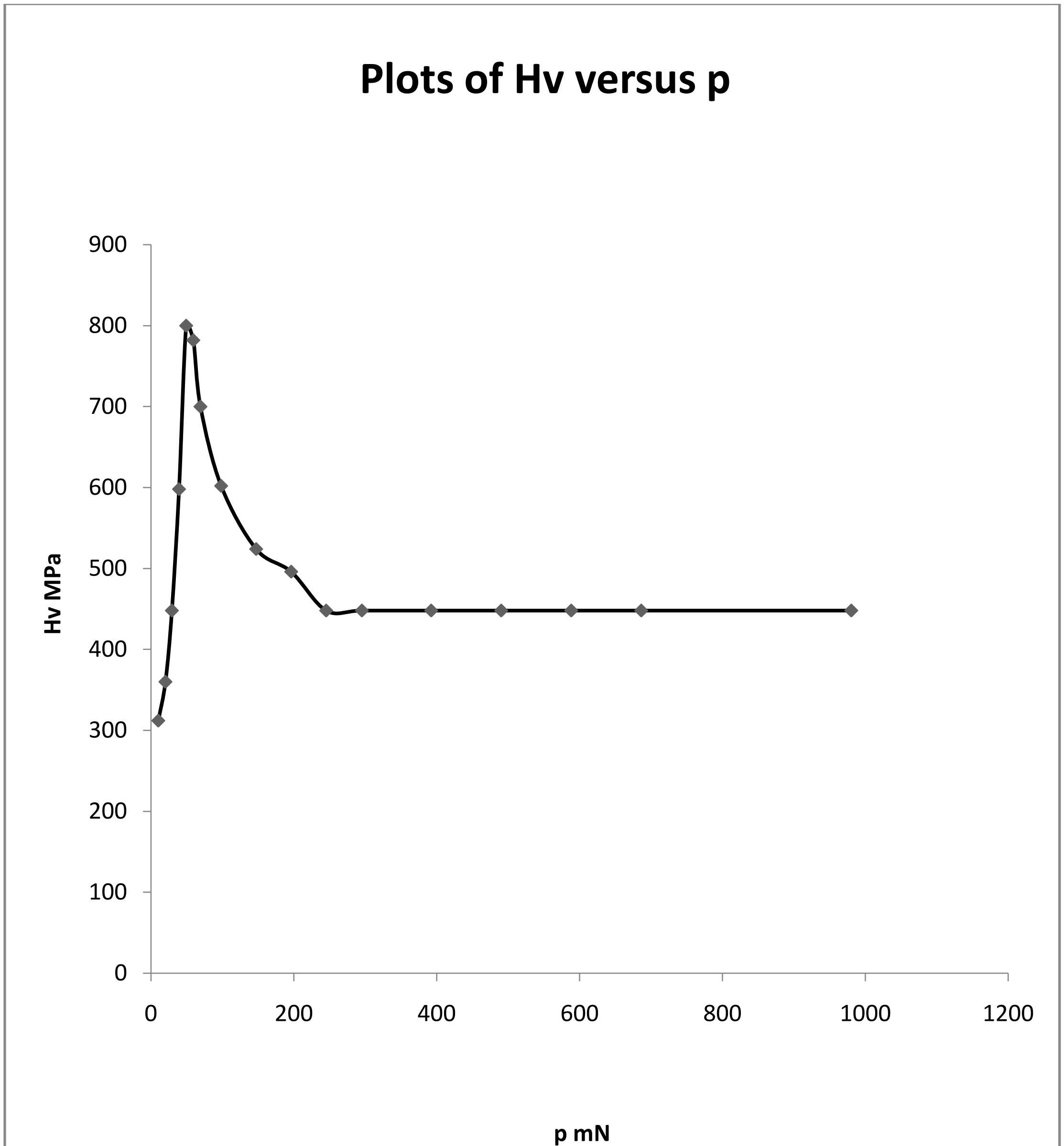

Figure –2 Plots of H_v versus p for Bi_2Te_3 crystals

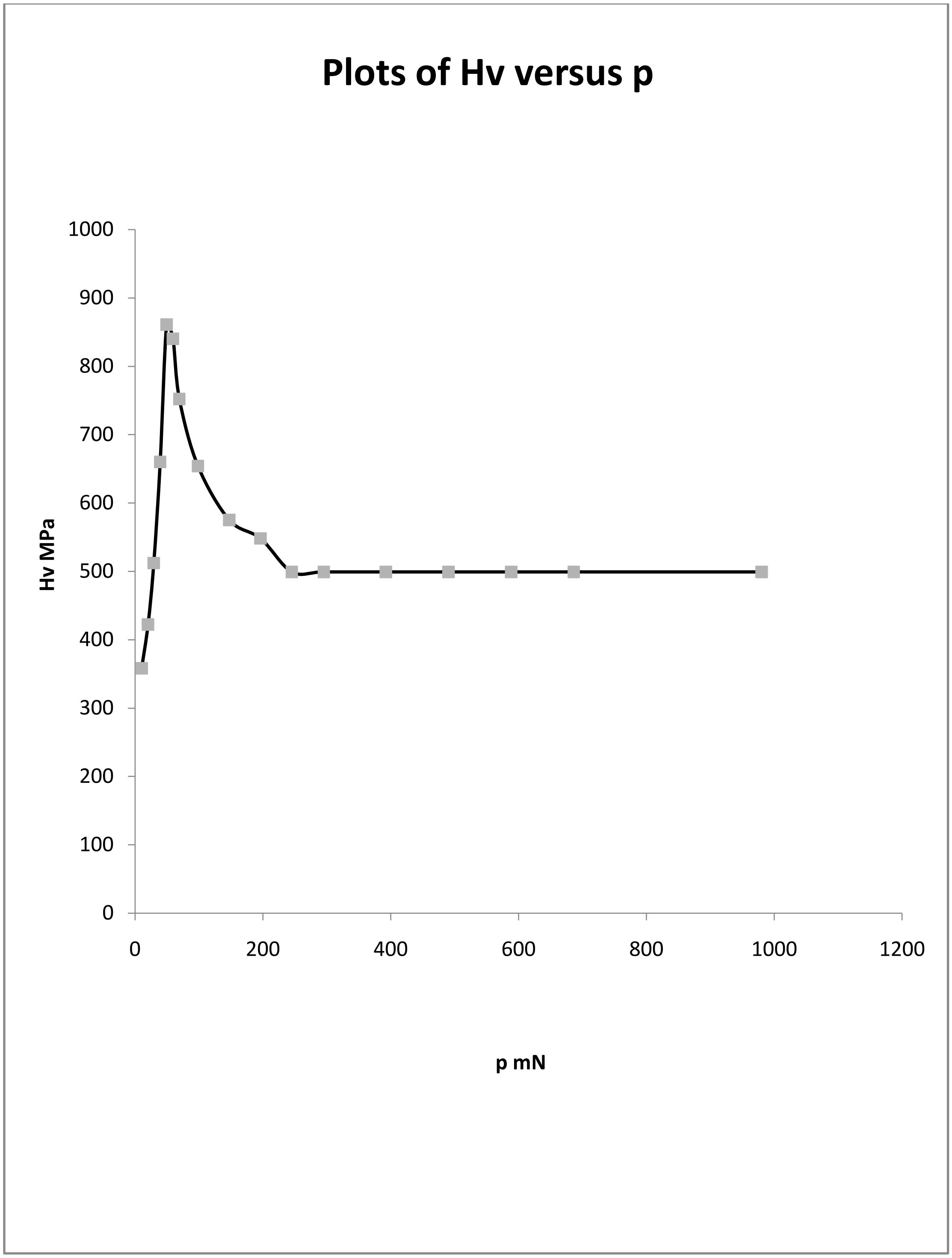

Figure –3 Plots of H_v versus p for $Bi_{1.95}Sb_{0.05}Te_3$ crystal

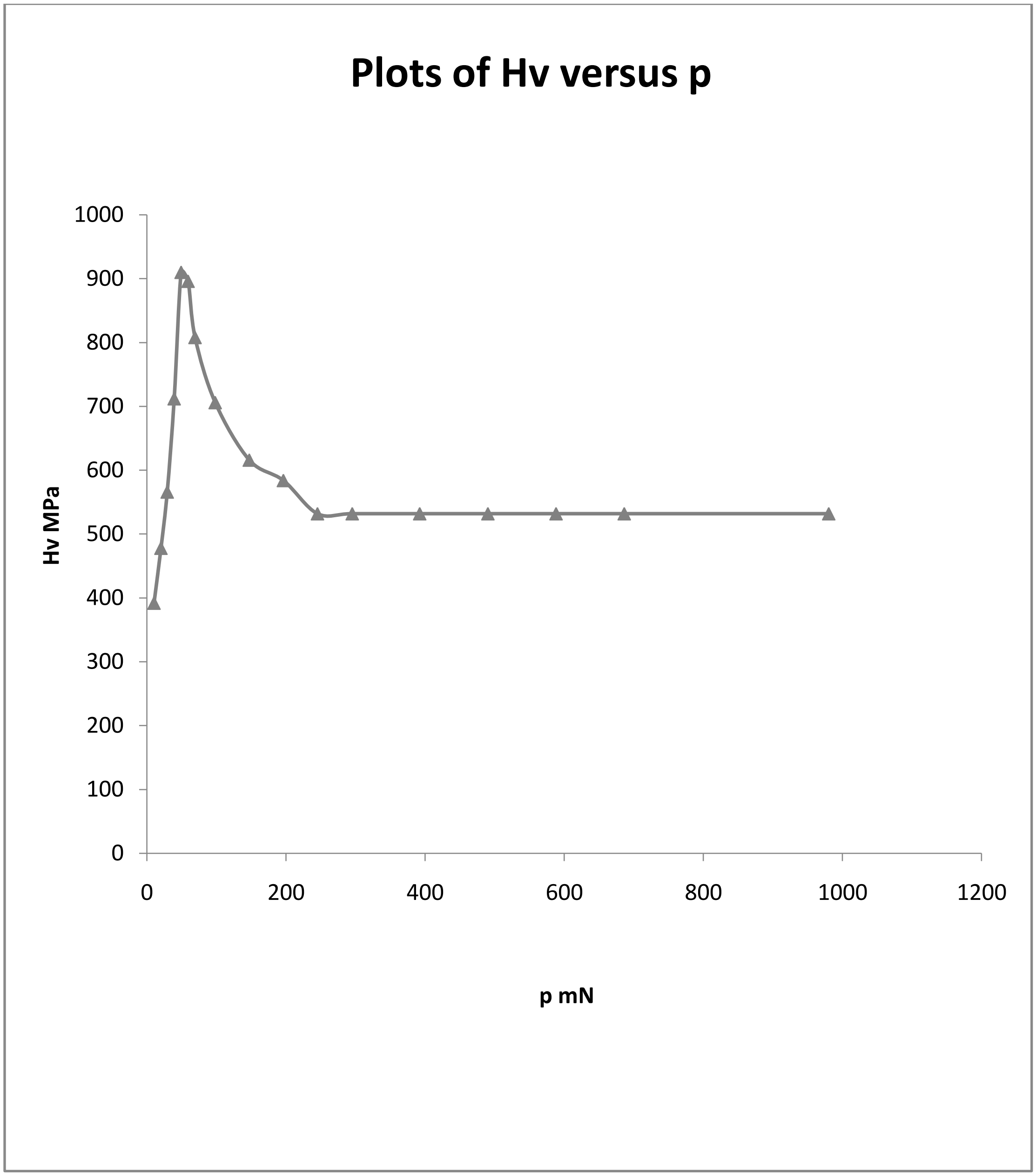

Figure –4 Plots of H_v versus p for $Bi_{1.90}Sb_{0.1}Te_3$ crystal

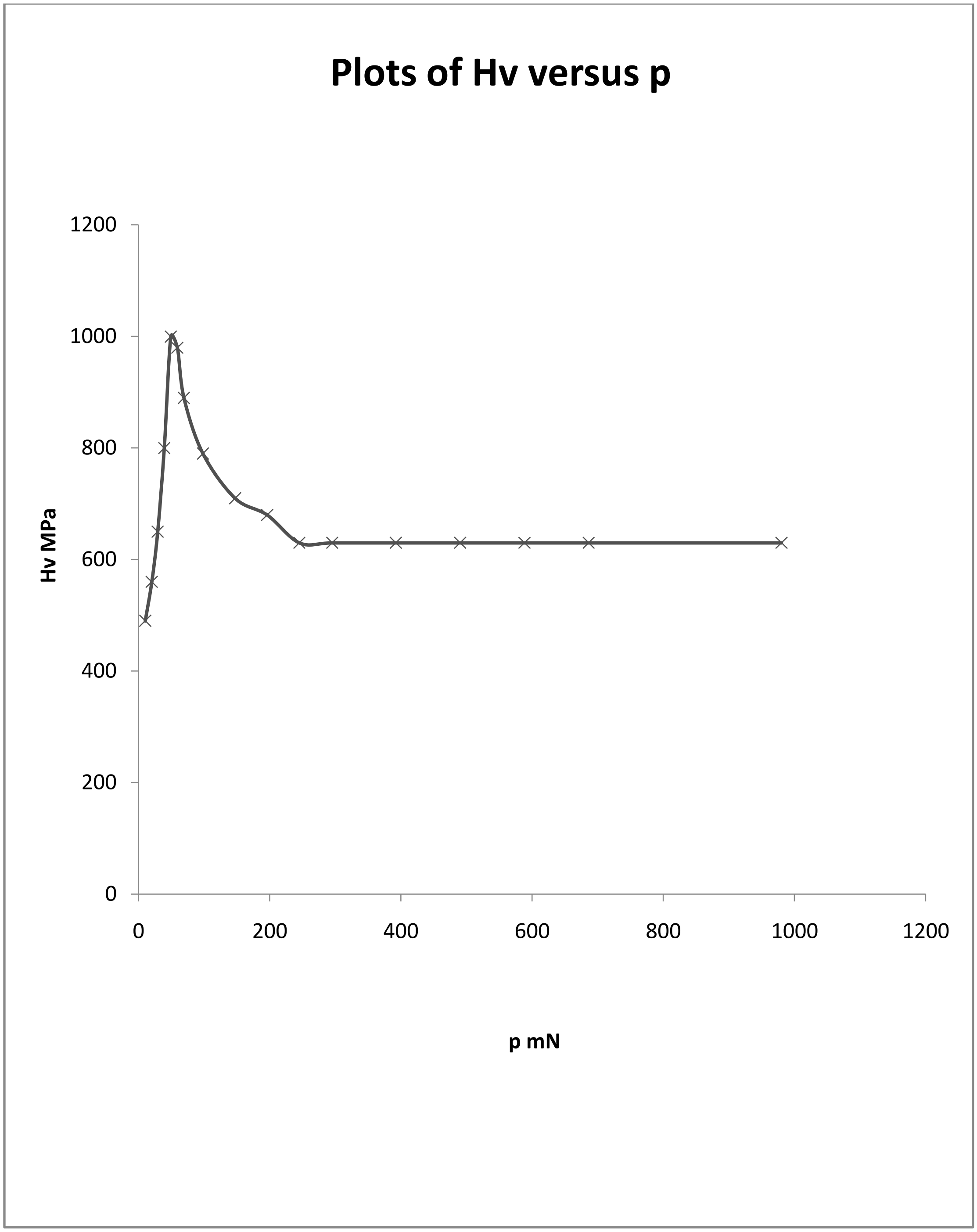

Figure –5 Plots of H_v versus p for $Bi_{1.80}Sb_{0.2}Te_3$ crystal

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 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.

The complexity observed in the load dependence of hardness closely parallels many reports on a variety of crystals [21-23]. Particularly, the low load range (i.e. 200 mN or less) defies the Kick's Law [24] which implies hardness to be independent of load. This dependence is normally ascribed to the strain hardening of the surface layers responding to the progressive penetration of the loaded indentor[21, 27]. The hardness peaks are in turn explained in terms of the resulting deformation-induced coherent regions. Beyond a certain depth of penetration, which corresponds to the expanse of the coherent region and to the load at the peak hardness, the indentor penetrates the virgin layers which easily favour nucleation and multiplication of dislocations [21, 26]. It is observed that the hardness is independent of load beyond 300 mN and represents the true hardness of the bulk of the crystal. Thus the characteristic hardness values of Bi_2Te_3,$Bi_{1.95}Sb_{0.05}Te_3$$Bi_{1.9}Sb_{0.1}Te_3$ and $Bi_{1.8}Sb_{0.2}Te_{3\ crystals}$ are 448, 499, 532 and 630, respectively. These values are consistent with the values reported by the authors in the case of the pure Bi_2Te_3 and $Bi_{1.8}Sb_{0.2}Te_3$ crystals, *viz*., 448 and 630 MPa, respectively [25,21]. 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)[28]

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

The hardness values of Bi_2Te_3,$Bi_{1.95}Sb_{0.05}Te_3$, $Bi_{1.9}Sb_{0.1}Te_3$ and $Bi_{1.8}Sb_{0.2}Te_3$ single crystals have been obtained to be 448, 499, 532 and 630, respectively. Further, with increasing Sb content, the hardness shows increasing trend as can be seen in Figure 6 as to be expected.

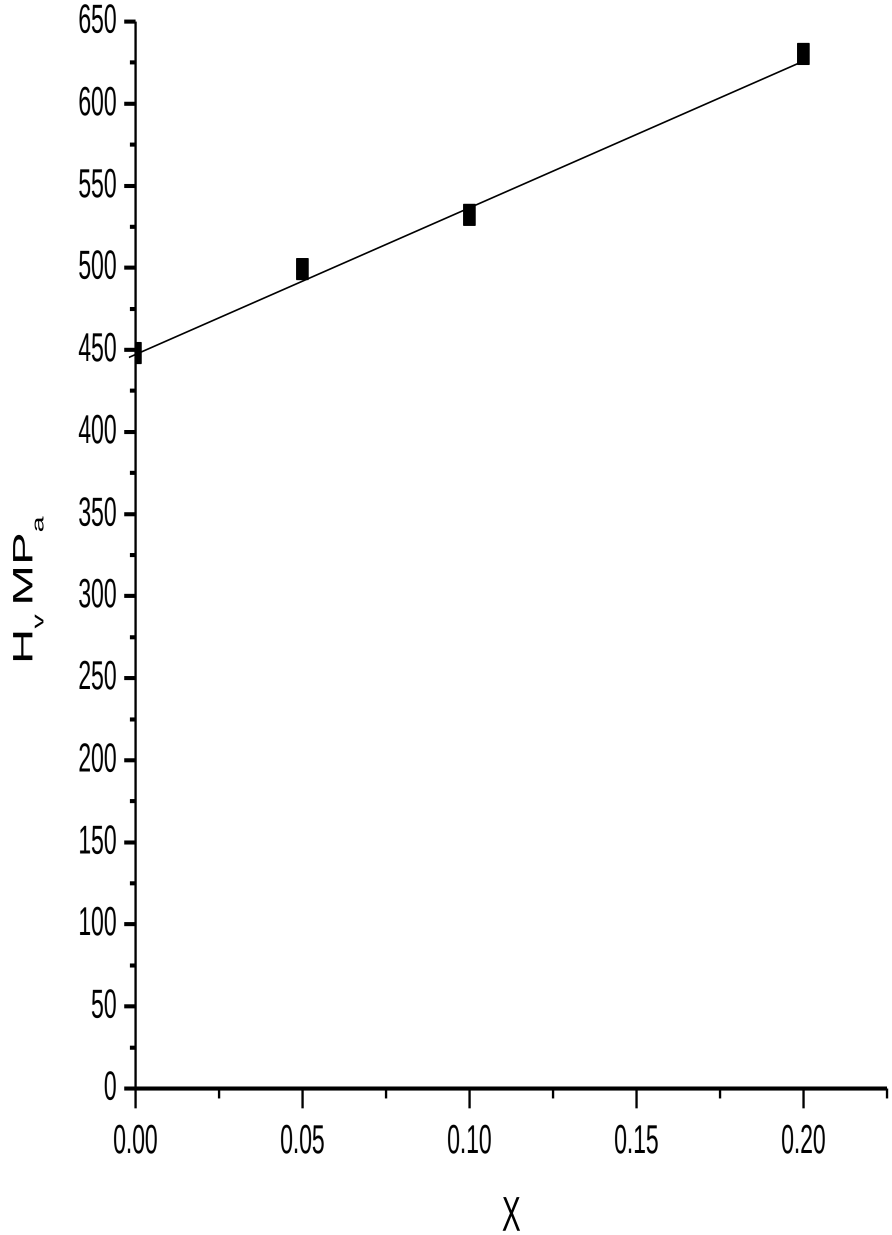

Fig. 6 Plot of Hv versus X

MEYER'S INDEX:

The Meyer's law is also useful to 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 [32]. This law can be written as

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

From the data of d and p, the plots of lnp vs ln d were obtained. These plots are shown in Fig 7,8,9and 10 for $Bi_{2-x}Sb_xTe_3$(x= 0, 0.05, 0.1, 0.2) crystals, respectively.

The plots of ln p versus ln d (where d =indentation diagonal length), follows the Meyer's law [33], $p=ad^n$ with different values of n in different load ranges (Fig 7-10). It is observed to be nearer to 2 in the high load range, reflecting the hardness saturation in this load range.

Whereas, the indentations at low loads seem strongly influenced by unpredictable load dependence to an extent that the linear relation is not followed as seen from the plots.

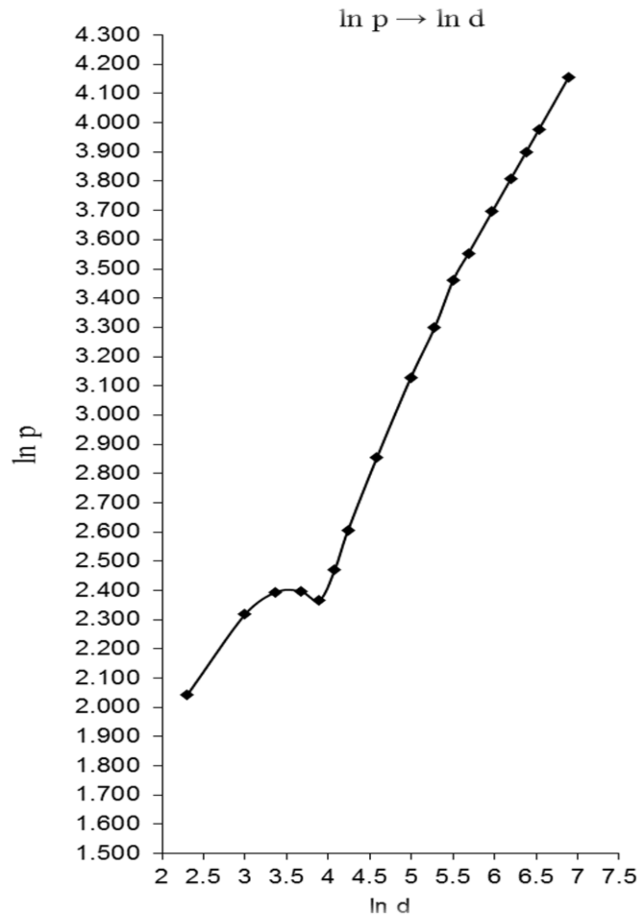

Figure -7 Bi_2Te_3

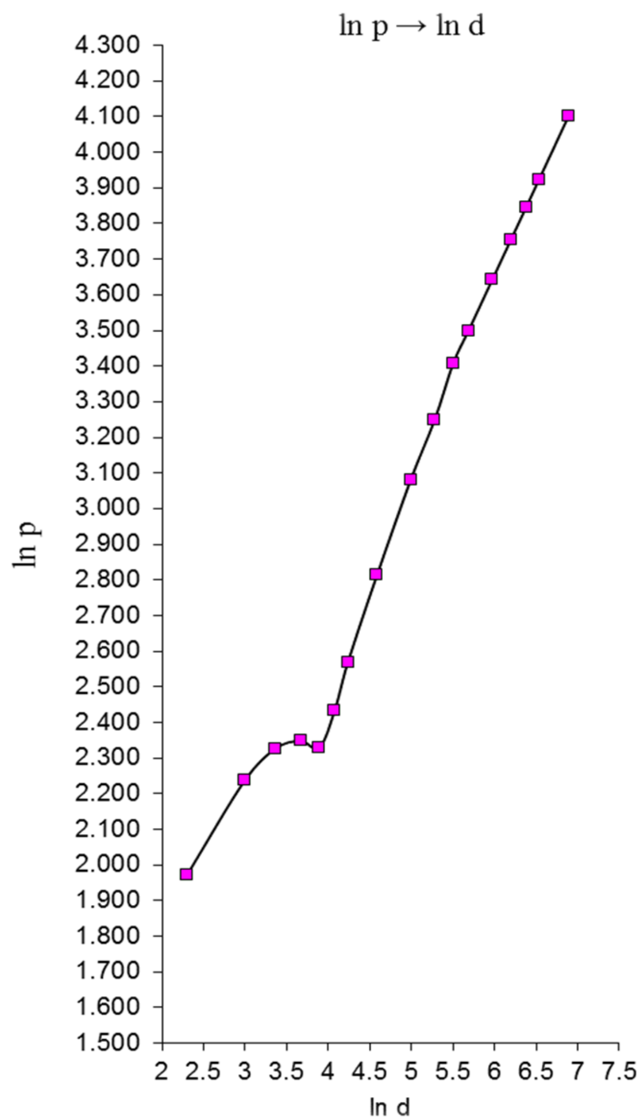

Figure -8 $Bi_{1.95}Sb_{0.05}Te_3$

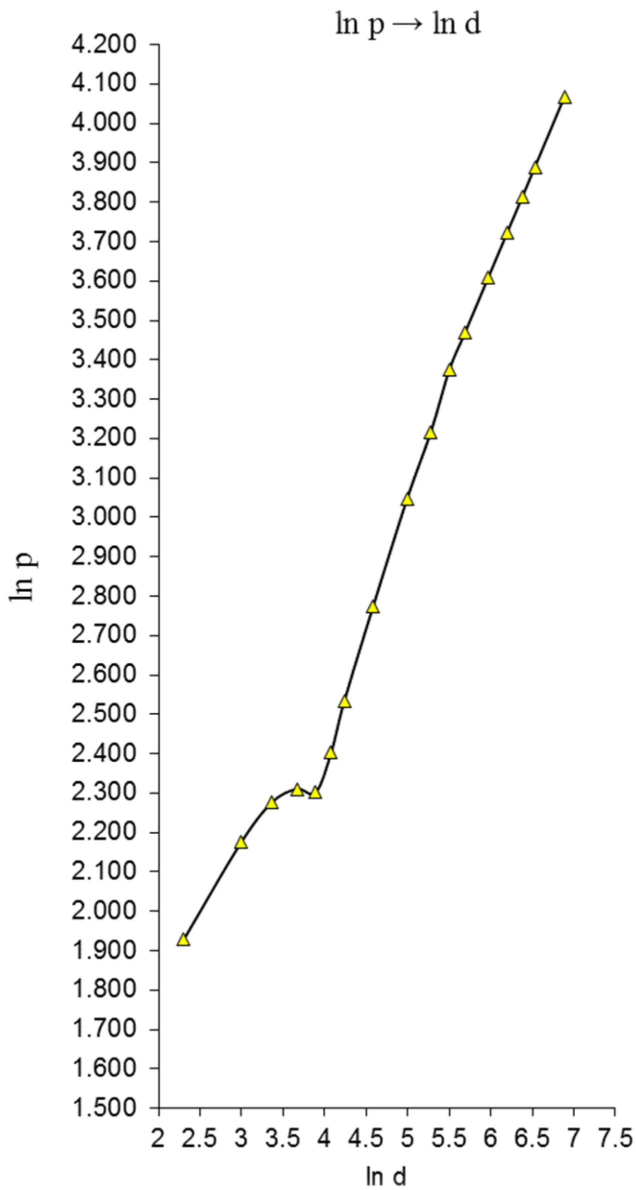

Figure -9 $Bi_{1.90}Sb_{0..1}Te_3$

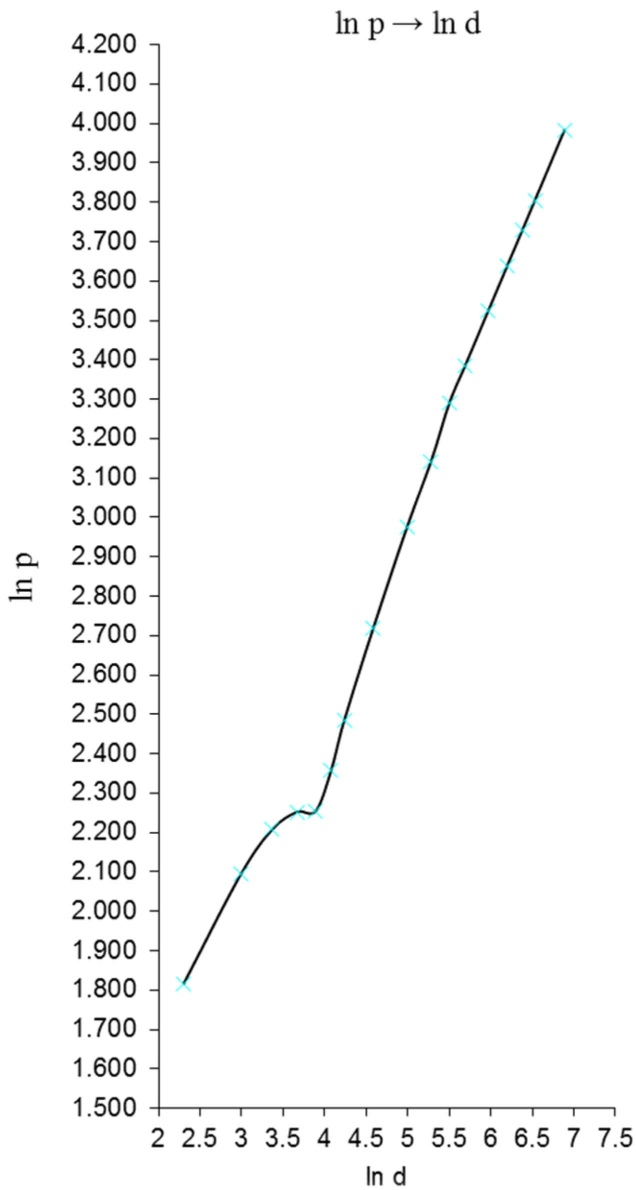

Figure -10 $Bi_{1.80}Sb_{0..2}Te_3$

CONCLUSIONS:

- The Hardness values of Bi_2Te_3, $Bi_{1.95}Sb_{0.05}Te_3$, $Bi_{1.9}Sb_{0.1}Te_3$, and $Bi_{1.8}Sb_{0.2}Te_3$ single crystals have been obtained to be 448, 499, 532 and 630, respectively.
- Microhardness is load dependent quantity and the variation is quite prominent in the low load ranges and only for sufficient high applied loads it becomes virtually independent of load.
- The hardness peaks observed in H_v versus load (P) plots may be explained in terms of deformation induced coherent regions.
- Due to work hardening, the crystal hardness increases. The Mayer index is not truly constant but may be different in different load ranges.

REFERENCES:

1. Shaw M.C., The Science of Hardness Testing and Its Research Applications, eds. J.H. Westbrook and H. Conrad (ASM, Ohio), (1973).
2. Tabor D., The Hardness of Metals (Oxford Univ.), (1951).
3. Bergsman E.B., Met. Progr., 54 (1948) 153.
4. Rostoker W., J.Inst. Met., 77 (1950) 1975.
5. Knoop F., Peters, C.G. and EnersonW.B., J. Res. Nat. Burstand, 23 (1939).
6. Bernhardt E.D., E.O.Z. Metallik, 33 (1941) 135.
7. Campbell R.F., Henderson O. and Danleavy M.R., Trans. ASM, 40 (1948) 954.
8. Taylor E.W., J. Inst. Met., 74 (1948) 493.
9. Buckle H., Rev. Retall., 48 (1951) 957.
10. Mott B.W., Ford. S.D. and Jones, I.R.W., A.E.R.E. Harwell Report, 1R, 1(1952) 17.
11. Grodzinsky P., Indust. Diam. Rev., 12 (1952) 209, 236.
12. Toman L. Jr., Nye W.F. and GelasA.J., 5th Int. Cong. Electron microscopy, 1 (1962) FF – 13.
13. BerzinaI.G., BermanI.B. and Savintsev P.A., Sov. Phys.Cryst, 9 (1965) 483
14. Gane N. and Cox J.M., Phill. Mag., 22 (1970) 881
15. Ivan'koA.A., Handbook of Hardness Data, ed. G.V. Samsonov, 3(1971).
16. Hanemann H., Z. Metallk., 33 (1941) 124
17. Mil'vidskiiM.G. and LinerL.V., Phys. Met. Metallog., 11 (1962) 96
18. BoyarskayaY.S., Zavod. Lab., 4 (1960) 477
19. Yoshino T., Bull. J.S.M.E., 8 (1965) 291
20. WallsM.G., Chaudhri M.M. and Tang T.B., J. Phys. D. Appl. Phys. (UK), 25, 3 (1992) 500 –7

21. Desai C. F., Soni P. H. and Bhavsar S. R., Ind. J. Pure and Appl. Phys., 37, 119(1999).

22. Buckle H., Rev Metal, 48,957(1951).

23. Bhatt V. P., Patel R. M. and Desai C. F., Cryst. Res. Technol. 18(1983)1173.

24. Mott B. W., Micro-indentation hardness testing (ButterworthsScientific Publications, London), Ch 1(1956).

25. Arivuoli D., Gnanam F. D. and Ramasamy P. s, J. Mater.Sci.Lett, 7(1988)711.

26. Jani.T. M, Pandya G. R. and Desai C. F., Cryst.Res. Technol. 29(1994)1.

27. Braunovic M., The Science of hardness testing and its research applications, Eds J H Westbrook and H Conard (ASN Ohio), (1973)329.

28. OnitschE.M., Schweiz. Arch. Angew. Wiss., 19 (1953) 320.

29. Buckle H., Med. Rev., 4 (1959) 49.

30. BochvarA.A. and ZhadaevaO.S., Bull. Acad. Sci. U.R.S.S., i3(1947) 341.

31. OnitschE.M., Mikroskopie, 2 (1947) 131

32. HanemannH.Z.Metallk, 33(1941) 124.

33. L. Meyer, Micro-indentation hardness testing (Butterworths Scientific Publications, London), Ch 4 (1956).