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# Vicker's microhardness of $Bi_{1-x}Sb_x$ ($x = 0.05$–$0.30$) crystals

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**Abstract** The solid–liquid interface of $Bi_{1-x}Sb_x$ crystal growth is very favorable for investigations of electron–phonon phenomena. Bismuth is a semimetal with high electron and hole mobilities. When Bi is doped with Sb in the range of 7–22 atomic percentage, it undergoes semimetal–semiconductor transition. Interest in Bi–Sb materials system has recently been stimulated due to promise of a new generation of thermoelectric materials based on these alloys. The starting materials used in this study, Bi and Sb, were both of 99.999% purity. The authors have studied microhardness of these crystals with the above said composition range. The crystals were grown using Zone melting method with 0.35 cm/h growth speed and 25 zone passes. 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. Microhardness indentation tests were carried out on the cleavage planes (111) of the $Bi_{1-x}Sb_x$ ($x = 0.5$ to 0.30) crystals, using the Vickers diamond pyramidal indenter. The results of Vickers microhardness studies on $Bi_{1-x}Sb_x$ ($x = 0.05$, 0.10, 0.15, 0.20, 0.25, 0.30) are presented in this paper.

## Introduction

Considerable attention has been given recently to the alloys of bismuth and antimony because they not only possess unusual thermoelectric and thermomagnetic effects at cryogenic temperatures but also possess semiconducting properties. Several research groups have investigated the use of Antimony as a surfactant during the growth of III–V compound semiconductors. Bismuth and antimony have rhombohedral structures at low antimony concentration, the alloy has metallic nature and becomes more and more semimetal with antimony concentration exceeding about $x = 0.1$. It is found that the Fermi energy of the alloy decreases with the increase in antimony concentration. The $Bi_{1-x}Sb_x$ alloy system can be either a semiconductor or a semi-metal depending on Sb concentration [1–8]**.** They have small energy band overlap between the conduction and valence bands, high carrier motilities, and a small effective mass. Because of these characteristics, Bi and Sb have frequently been used for quantum-size effect studies. Hardness testing is one of the mechanical properties to check nature of the metal and nonmetal materials. There have been various studies on the bulk and thin film characteristics of Bi–Sb including optical, electrical, and mechanical properties [1–8]. However, there is hardly any work reported in the literature on the microhardness of Bi–Sb. The present paper reports the results of the microhardness of $Bi_{1-x}Sb_x$ ($x = 0.05$, 0.10, 0.15, 0.20, 0.25, 0.30) single crystals.

## Experimental techniques

Bismuth and Antimony each of 99.999 % purity (5 N purity) were purchased from Nuclear Fuel Complex, Hyderabad, India. The stoichiometric amounts of the materials were weighed accurately up to 10 μm using a semi-microbalance and filled in a quartz ampoule of about 10 cm length and 1 cm diameter. The quartz tube was then

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vacuum-sealed at a pressure of about $10^{-4}$ Pa and it was kept in the alloy-mixing furnace. In this mixing unit, the material was mixed in the molten state for about 48 h by rotating the tube at 10 rpm at 630 °C for thorough mixing. The rotation of the tube was stopped and the material was further kept in the molten state for further 24 h in order to ensure homogenization and complete reaction in the molten charge. It was then slowly cooled to room temperature. This process usually produces fairly homogeneous alloy. The ingot so prepared was subjected to growth by zone melting.

The $Bi_{1-x}Sb_x$ ($x = 0.05$, 0.1, 0.15, 0.20, 0.25, 0.30) alloys prepared as discussed above were used for growing single crystals by zone melting method. The starting ingot was about 6 cm in length and 0.8 to 1 cm in diameter. First the ingot was zone levelled. The temperature gradient across the two solid–liquid interfaces was obtained to be about 65 °C/cm by controlling the furnace temperature within ±1 °C, giving a zone length of about 1–2 cm.

To level off impurities, 10–25 passes in alternate directions were given and finally the last pass was used to obtain self-nucleated single crystals. To obtain good quality crystals, it was found necessary to give sufficient time to the first molten zone before starting the zone travel to achieve stable conditions. Single crystals grown by the zone melting method after 25 zone leveling passes at the growth speed of 0.35 cm/h were used for the microhardness study. The crystals have good planar cleavage along (111) and the tests were carried out on the freshly cleaved (111) surfaces of the 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 a least count 0.19 μm. The indentations using Vickers' pyramidal diamond indenter were made at different loads ranging from 1 to 160 gm for fixed azimuthal orientations of the indenter to avoid anisotropic variations as described earlier. The indentation time was kept constant at 30 s.

The Vickers hardness is defined as the ratio of applied load to the pyramidal contact area of indentation and it is calculated as

$$H_v = \frac{1854P}{d^2}\ \mathrm{Kg/mm^2} \quad (1)$$

where

$H_v$ = Vickers' microhardness in Kg/mm$^2$
$P$ = Applied load in gm
$d$ = Mean diagonal length of the indentation mark in μm

The indentation mark is geometrically similar whatever be 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 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, are known as microhardness values. Though, the limit load is not sharply defined, practically the hardness may achieve a constant value for loads in the range 20–50 gm and beyond, depending on the material.

## Results and discussion

Figure 1 shows the plots of Vickers hardness $H_v$ versus load $P$, obtained at room temperature, for $Bi_{1-x}Sb_x$ ($x = 0.05$). 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.

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 [9]. 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 undeformed bulk of the material and hence independent of load. Even for surfaces which require

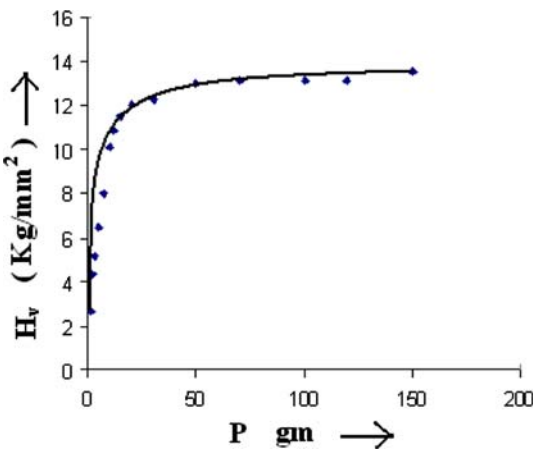


**Fig. 1** Plot of $H_v$ vs. $P$ ($Bi_{0.95}Sb_{0.05}$)

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.

On the basis of depth of penetration of the indenter, the observed variation of hardness with load in the plot of $H_v$ vs. $P$ 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. In the present case this depth of penetration has been estimated to be about 7–18 μm as the saturation hardness varies from 50 to 12 kg/mm$^2$ for $x$ varying from 0.30 to 0.05. The bulk characteristic hardness is usually represented by the value in the saturation region [10, 11].

The hardness obtained from these data is plotted in Fig. 2 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.

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, $P$ = applied load, $d$ = diagonal length of the indention mark in μm, and $a$ = material constant. Load dependence of hardness is reflected in the deviation of the value of $n$ from 2 [12–14]. This law can also be written as

$$\ln P = \ln a + n \ln d \tag{2}$$

From the data of $d$ and $P$, the plots of ln $P$ versus ln $d$ were obtained. These plots are shown in Fig. 3. The slope of the graph gives the value of Meyer's index.

The values of Meyer index obtained in the present case are mentioned in the following table.

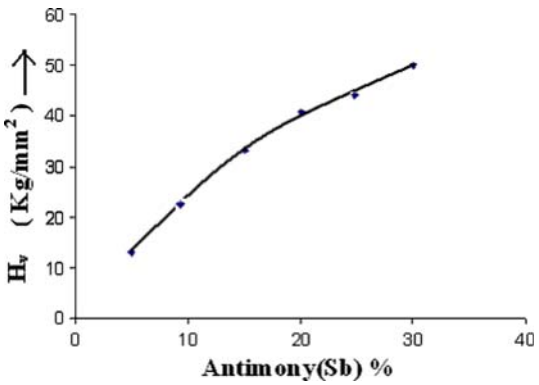


**Fig. 2** Plot of $H_v$ vs. Sb concentration

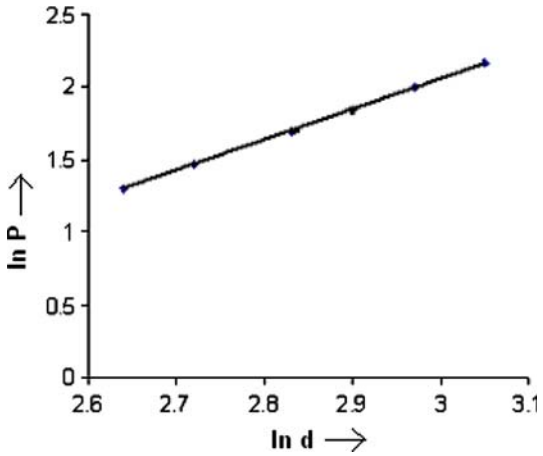


**Fig. 3** Plot of ln $P$ vs. ln $d$ ($Bi_{0.95}Sb_{0.05}$)

| Material | Meyer index |
|---|---|
| $Bi_{0.95}Sb_{0.05}$ | 2.11 |
| $Bi_{0.90}Sb_{0.10}$ | 2.09 |
| $Bi_{0.85}Sb_{0.15}$ | 2.05 |
| $Bi_{0.80}Sb_{0.20}$ | 1.98 |
| $Bi_{0.75}Sb_{0.25}$ | 2.02 |
| $Bi_{0.70}Sb_{0.30}$ | 1.98 |

## Conclusions

1. The hardness of the crystals under study increases with increasing Sb concentration which may be a result of covalent bond dominating in this range of semiconducting compositions.
2. The hardness depends on load, increasing with load before reaching the saturation at load of around 50 gm or correspondingly at the indenter penetration depth ranging from 7 to 18 μm depending on the Sb concentration. This increasing trend of hardness with load can be attributed to the surface hardening phenomenon.

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