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MICROHARDNESS STUDIES OF GROWN CRYSTALS

6.1 Introduction

The mechanical behaviour of a crystal is of paramount importance in technological applications. The hardness of the material is identified as an important mechanical property. The hardness measurement is treated as an efficient technique of providing information about the elastic, plastic, viscous and fracture properties. Although hardness is one of the properties of which we are most conscious, it is very difficult to define it precisely so as to include all the various characteristics of a material which have been referred to as hardness. The precise definition depends entirely on the method of measurement, which will determine the scale of hardness obtained[1]. The suggestions by Ashby[2] probably is the best general definition that can be given as 'hardness is a measure of the resistance to permanent deformation or damage'. Shockley[3] and Buckley[4] point out the possibility of investigating various properties by means of microhardness measurements. Hardness of the crystals is obviously related to the crystal structure of the material or in other words, the pattern in which the atoms are packed and the electronic factors operating to make the structure stable. Indentation technique have been used by a number of

investigators[5,6,7] to study the glide deformations, isotropy or anisotropy, cracks, grain boundary hardening, irradiation effect and environment of dislocation mobility of various crystals[8,9] .

Microhardness values on different cleavage planes or faces of the same material will also differ. The Vickers microhardness values of [100] and [110] faces of ADP are 69 and 73. [100], [110] and [120] faces of K_2SO_4 are 95, 100 and 130 respectively. Grain boundary hardening in oriented niobium crystals with symmetric boundaries has been determined by Chou[10] et al by microhardness measurements. Number of investigators have utilised the doping technique and other stoichiometric combination of different components to re-tailoring the physical properties in particular the hardness of the material[11,12]. Joshi[13] et al have reported the effect of quenching on Vickers hardness of mesolite crystal. Cahoon[14] et al have arrived at an expression connecting the strength of the material and Vickers hardness number, which helps to calculate the yield strength of the materials. There exists a correlation of hardness with energy gap (E_g) for the III-V compounds[15] and V-VI compounds[16]. For the materials quality design, the fracture and toughness are very important. Crack possibility under loading condition can be determined by the analysis of the deformation fracture mechanics of the indentation process by considering an equilibrium condition. A more accurate measurement of Vickers hardness number has been done by Gillmann[17]. Brittleness index is calculated by taking the ratio between hardness and toughness. An arbitrary scale for determining the brittleness number has been devised by Glazov and Vigderovicks[18].

Rare earth mixed hydrogen selenite crystals is of a layered structure with space group $P2_1/c_1$, (C^5_{2h}). It is observed that these materials have low hardness values. Microindentation test is the best method of studying the deformation of the material. Many authors have reported the microhardness measurements on various single crystals using Vickers indenter[19,20,21]

Out of many types of hardness test, the most suitable one in the present case is Vickers test.

6.2 Vickers test

In Vickers hardness test, a square based pyramid is used for which the apex angle included between opposite faces is ideally 136°. Pyramid indenters are said to be best suited for hardness tests due to two reasons[22].

(i). The contact pressure for pyramid indenter is independent of indentent size.
(ii). Pyramid indenters are less affected by elastic release.

Vickers pyramid has a square shaped base and depth of indentation corresponds to $1/7^{th}$ of the indentation diagonal (fig.6.1). The longitudinal and transverse diagonal is in the ratio 7:1 and the depth of indentation is about $1/30^{th}$ of the longitudinal diagonal. Here hardness is defined as the ratio of the load applied to the surface area of the indentation. The Vickers hardness number H_v, (Diamond pyramid number of DPN) is defined as

$$H_V = \frac{2LSin\frac{1}{2}(136^o)}{d^2}$$

$$H_V = \frac{2LSin(68^o)}{d^2}$$

$$= 1.8544\ L/d^2\ kg/mm^2$$

In microhardness tests, usually using the loads in the range of 1-100 gms, the size of the impression is typically a few microns (10^{-3} mm) across; a powerful microscope is employed to measure it. The quality of the surface of the specimen is very important for the indentation impression to be visible. Hardness value is independent of the depth of the penetration as expected.

Since all the indentations are geometrically similar, the time for load application is automatically adjusted as 20 seconds. The loads usually used are in the range from 1gm to 100gm to give an indentation which can be easily measured 1μm across.

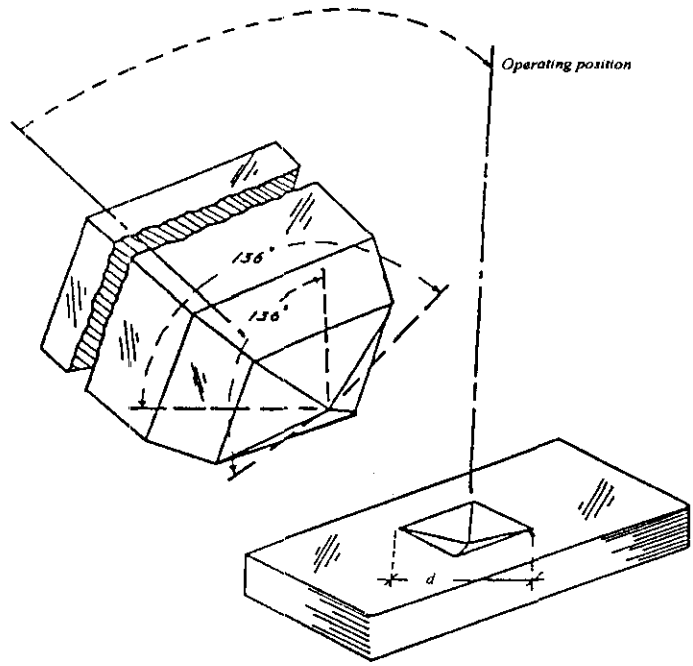

Fig. 6.1. Vickers pyramid having square shaped base and depth of indentation corresponds to $1/7^{th}$ of the indentation diagonal

6.3 Corrections in measurements

In the microhardness test many factors contribute to error terms. This can be grouped into three.

1. Deviation of loading from the nominal value. This may be due to the incorrect calibration, faulty operation of the machine, inertia, vibration effects and the time of indentation factor which is closely linked with vibration.

2. Incorrect profile of indenter, this includes a deviation from the standard angle 136° between the faces of the indenter, faces which are not exactly flat and chisel tips. (ie. the faces do not meet at a point)

3. Lateral movement of the indenter; errors in loading.

A positive loading error results in a larger impression than would be given by the nominal load making the apparent hardness number, which is based on the nominal load, lower than the true value.

By definition the Vickers hardness number is given by

$$H_v = \frac{2LSin\frac{\alpha}{2}}{d^2}$$

For a given indenter Sin $\alpha/2$ is a constant, and therefore this can be written as

$$H_v = KL/d^2$$

If differentiated with respect to L,

$$dH_v/dL = K/d^2 = H_v/L$$

Thus for a maximum loading error of ΔL, the hardness error ΔH_v is given by

$$\Delta H_v/ H_v = \Delta L/L$$

This indicate that the percentage error in hardness decreases directly with increase in load. So it is better to use as high a load as possible.

If L_0 is a constant of loading error independent of L.

Then $H_v = K(L+L_0)/d^2$

If the hardness is independent of load

$d^2 = K_1 (L + L_0)$, K_1 is a constant

The measurement error in Vickers test is usually associated with inaccuracies committed in measuring the diagonals of impressions. The factors contributing to this are deformation of the edge of the impression, non-uniformity of illumination, parallax, inaccuracy in calibrating the loading mechanism, errors in taking readings

etc. All these factors have a cumulative effect in the error in determining the diagonal of an impression.

The average microhardness

$$H_v^{av} = \frac{1}{n}\sum_{i=1}^{n} H_v^i$$

Where 'n' is the number of measurements and H_v^i is the individual measurements. The mean square deviation is determined from

$$\sigma^2 = \frac{1}{n}\sum (H_v^i - H_v^{av})^2$$

The accuracy of determining hardness is given by

$$\Delta = \frac{\alpha^2}{n\left(\frac{\sigma}{H_v^{av}}\right)^2}$$

where α is the parameter and is equal to 1.65.

6.4 Micro-indentation studies at low loads

Micro-indentation study at low load will show considerable disagreement in hardness number compared to high loads. It is seen that in some cases the hardness value increases with load and in some others hardness value decreases. It is also reported that in some cases no variation is observed. An oscillatory behaviour is sometimes observed in some cases.

When micro-indentation test is carried out at low loads some precaution has to be taken for avoiding errors in measurements. Errors are introduced due to several reasons, like loading, time of indentation, preparation and maintaining of specimen, limitation of the measuring device and influence of the indenter over the neighbouring impressions. Along with these factors, the isotropy, planarity or bulkiness should also be considered.

To avoid error in loading, it is better to calibrate load pick-up with the test load, before the experiment. The fact that there is no error in loading is checked at the end of the experiment by confirming that the plot drawn d^2 and P pass through the origin. The top loading mechanism of the instrument gives less chance for introducing errors due to inertial loading. Time of indentation, does not affect the size of the impression. However it is reported[23] that a minimum period of 10 seconds is essential to arrive at standard condition of loading. The specimen preparation and mounting of the sample need a lot of attention. If the specimen surface is away from the ideal condition it may affect the result. It is better that successive indentation may be made on the same sample and there should be a separation of at least three times the diagonal impression between the two pits and the depth should not exceed more than one tenth of the thickness of the specimen.

Vickers static micro-indentation tester was used to study the hardness of gel grown single and mixed crystals of rare earth hydrogen selenites. A hardness tester (Leitz Miniload-2) fitted with a diamond pyramidal indenter attached to a metallurgical microscope is utilised for the measurements. The diagonal of the pyramidal impression was measured with a calibrated ocular eyepiece at 500-fold magnification. The load P is varied from 5 to 100gm and the time of indentation kept constant at 20 seconds. All the indentations are done at ambient condition. The diamond indenter has been applied perpendicular to layer planes (parallel to c axis of the crystallographic axis)

The indentations were made at different sites of the crystals and the separations between the successive impressions are made. Care has been taken that the distance between two impressions is less than three times the diagonal of the pyramid impression. A good number of trials have been made on each crystal for each load and the average values of indentation marks were recorded. Diagonal length measurements have been taken only for similar shaped impressions.

The microhardness at each load

$$H_v = 1.8544\ P/d^2\ kg/mm^2$$

Where H_v –Vickers microhardness number

P – load in kg, d – diagonal length of impression in μm.

6.5 Results and discussion

6.5.1. Variation of hardness with load

The gel grown crystals of good quality and in size are selected for the hardness measurements studies. At large loads the crystal show brittle behaviour. The variation of the hardness with different stoichiometric ratios shows interesting result. All the grown mixed and mono rare earth hydrogen selenite crystals show a high hardness number (Hv) at low load and low Hv at high load.

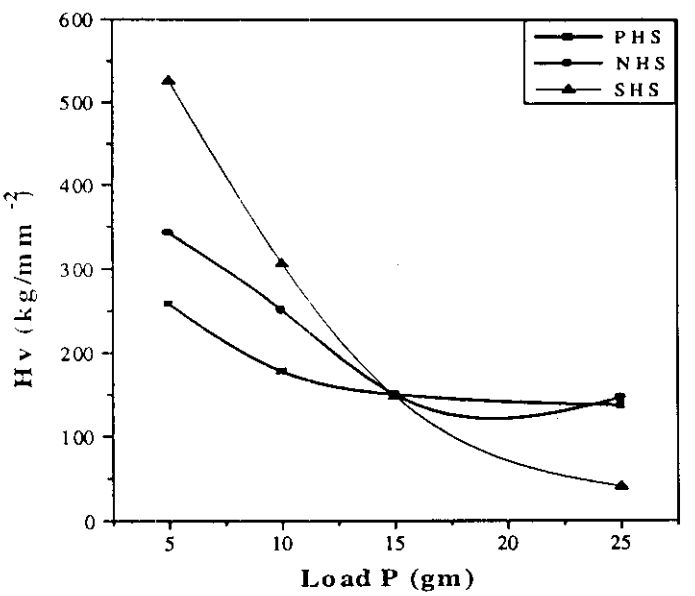

Fig. 6.2. Variation of hardness Vs load of mono rare earth hydrogen selenite

The indentation have been done on all grown crystals and the studies are conducted for various load values on various stoichiometric combinations of mixed hydrogen selenite crystals. A plot of hardness number versus applied load for mono (single) rare earth hydrogen selenite crystals is shown (fig. 6.2). This shows that the value of hardness of the crystal decrease from samarium hydrogen selenite crystals to

praseodymium hydrogen selenite crystal at low load. The dislocation density of the gel grown crystals are very low[24]. Out of PHS, NHS and SHS; PHS shows lowest hardness at low load and the variation with load is not that prominent. Variation of the hardness with load has been given in fig. 6.2.

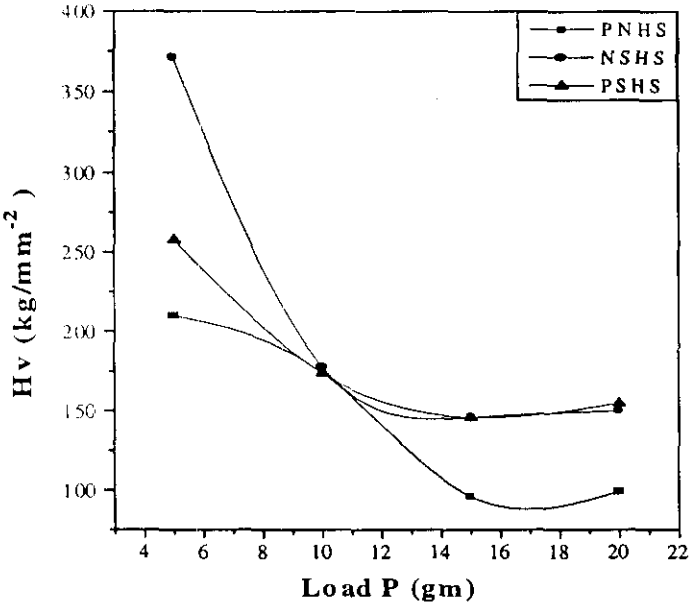

Fig. 6.3. Variation of hardness Vs load of mixed rare earth hydrogen selenite

In the case of mixed hydrogen selenite with a particular stoichiometry, the variation of hardness number with a load is given in fig. 6.3. At low load as in the case of mono rare earth crystals mixed crystals also show a similar variation. When the load increases the hardness decreases and attains a constant value. For the mixed crystals of stoichiometric combination of (50:50) the value of hardness decreases from NSHS to PNHS crystals at low load.

6.5.2 Influence of rare earth on the hardness of mixed crystals

Fig. 6.4–6.6 show the variation of the hardness number with the stoichiometric changes of rare earth element in the mixed crystals. The experiment has been done for 10gm load in all cases.

In the case of PSHS crystals in which the percentage of praseodymium is varied the graph (fig. 6.4) show maximum hardness value at equal percentages of components.

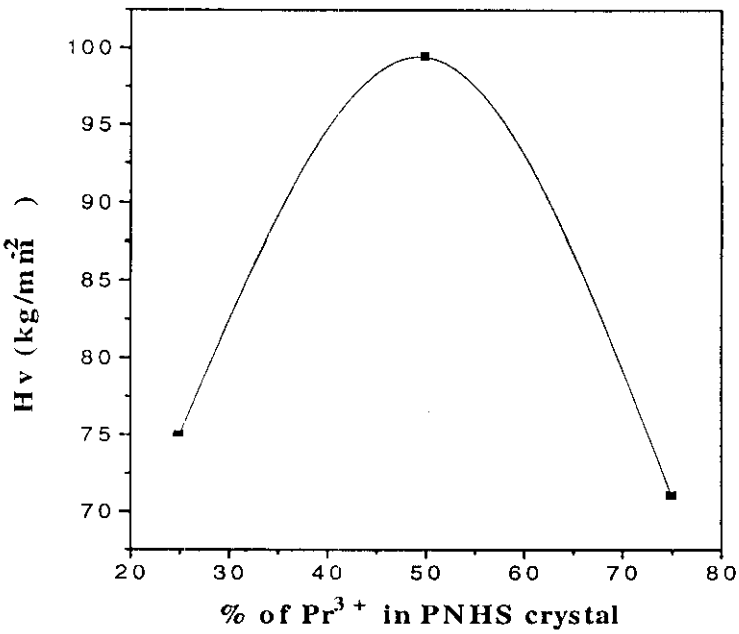

Fig. 6.4. Stoichiometric variation of hardness Vs load in PNHS crystal

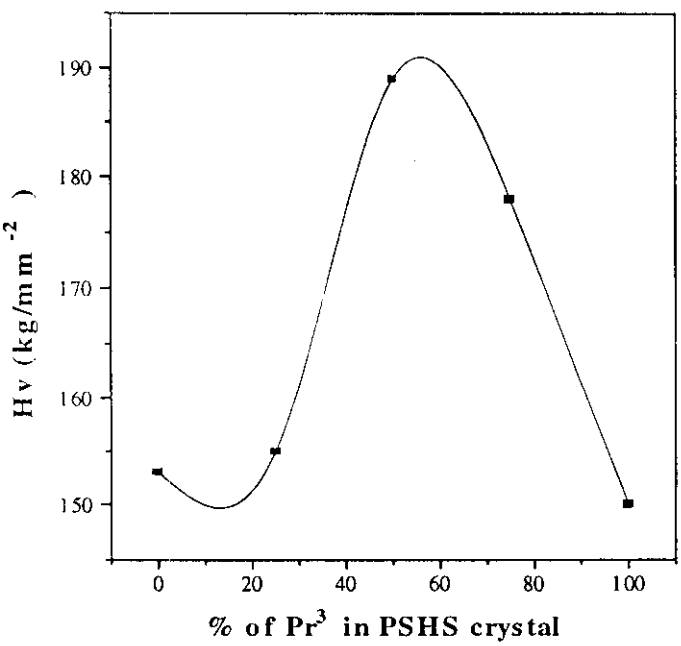

Fig. 6.5. Stoichiometric variation of hardness Vs load in PSHS crystal

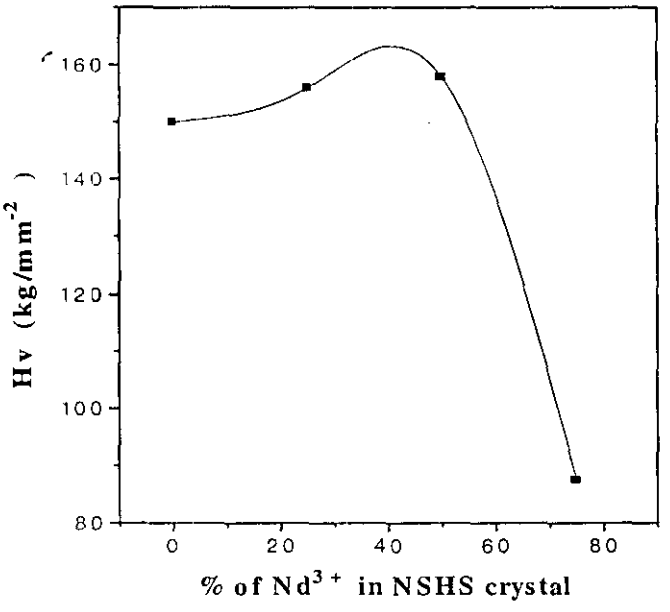

Fig. 6.6. Stoichiometric variation of hardness Vs load in NSHS crystal

6.6 Conclusion

The observations on mixed crystals show that the hardness depend on the stoichiometric ratio of the component elements. At constant load the hardness increases to a maximum value at equal percentage of the components and then decreases to a minimum level when the other component is predominant. This is true in all cases. The minimum hardness agrees with the early experiments on mono component crystals.

The fact that the hardness reaches the maximum value at 50:50 stoichiometric composition of the components may be explained as follows. When components in a lower concentration the minority atoms might be going to the structure replacing other component and as an interstitial. When the components are in equal proportion atoms will get a chance to arrange in an orderly way since it will have minimum energy configuration. Interstitials may be minimum in this particular case.

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