Chapter 6
MICROHARDNESS

Abstract
Microhardness is the only mechanical test that can be employed when the material is not available in substantial quantities. The microhardness of the samples were measured using Vickers indentation method. The hardness number is calculated using the relation

$$H_v = \frac{1.854PKg \ mm^2}{d^2}$$

where \(d\) is the diagonal length of the indentation and \(P\) is the load.

Microhardness of the grown crystals increases with the load \(P\) and cracks start propagating from the indentation mark when loaded beyond 50 gm. The work hardening coefficients, \(n_1\) (low load region) and \(n_2\) (high load region) from the slopes of \(\log P\) vs. \(\log d\) graph were also determined. Work hardening coefficients \(n_1\) and \(n_2\) were found to be greater than 2, giving the inference that the grown crystals belong to soft materials.
6.1 INTRODUCTION

The mechanical behaviour of a crystal is of paramount importance in technological applications. The simplest mechanical property test that can be performed on the grown crystal samples is the microhardness measurements. It is the only mechanical test that can be employed when the material is not available in substantial quantities. 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. Hardness is a measure of the resistance to permanent deformation or damage. Shockley et al.\textsuperscript{1} and Buckley\textsuperscript{2} pointed 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.
6.2 VICKERS HARDNESS TEST METHOD

The microhardness of the samples were measured using Vickers Indentation method. Vickers hardness tester is the equipment that is indispensable to metallographic research, product quality control, and the development of product certification materials. This equipment can be used to measure the hardness of small parts and metallic structures used in precision equipment, processed surface layers, metal plating layers, etc.

This type of measurement must be performed on a limited area with small damage to the area being measured, and must yield extremely reliable results. A hardness tester (Leitz Mini load 2) fitted with a diamond pyramidal indenter attached to an incident light microscope was used for study. The diamond indenter is in the form of a square pyramid, opposite faces of which make an angle 136° with one another. The indenter can be pressed on the sample under a load P of 5, 10, 15, 25, etc. grams. The duration of the indentation time was kept constant at 10 seconds. Hardness is computed from the size of the impression left on the sample surface after indentation and hence includes the effects involved in the material response to the indentation pressure during loading and relaxation during unloading. For each load several
indentations were made and the average value of the diagonal length of the indentation mark was considered to calculate the microhardness. The impression is of a square pyramid and has a superficial area of \( \frac{d^2}{2 \sin 68^\circ} \) where \( d \) is the diagonal length of the indentation. The area of impression is related to hardness as Vickers Hardness number \( H_v \).

\[
H_v = \frac{\text{load}}{\text{area of impression}}
\]

\[
= \frac{2P \sin 68^\circ}{d^2} \ \text{g} \times \text{\mu m}^2
\]

\[
= \frac{1.854P}{d^2} \ \text{Kg} \ \text{mm}^2
\]

\[\text{.........(6.1)}\]

where \( P \) is in kilograms and \( d \) is in millimeters. The data obtained for \( P \) and \( d \) can be analyzed by Mayer’s equation \(^4\)

\[P = a \ d^n\]

where ‘\( a \)’ and ‘\( n \)’ are constants for the material under test. By using plots of \( \log P \) vs. \( \log d \), constant \( n \) called Mayer index can be calculated for the crystal plane under study. The value of \( n \) represents the capacity for work hardening. Kick’s \(^5\) analysis for hardness postulates a constant value of \( n=2 \) for all indenters that give impressions geometrically similar to each other.
Fig: 6.1 Vickers Hardness Test Method
6.3 MICROHARDNESS MEASUREMENTS OF THE PURE AND MIXED RARE EARTH OXALATE CRYSTALS

Perfectly plane, transparent crystals of YOx, YBaOx, YCuOx, YBaCuOx, PrBaCuOx, NdBaCuOx, GdBaCuOx and DyBaCuOx were grown by using the respective rare earth chlorides in the feed solution. Indentations were carried out using a Vickers pyramidal indenter for various loads ranging from 5 to 50 gram on the crystals. The duration of the indentation time was kept constant at 10 seconds. In all experiments, the distance between two indentations was kept five times greater than the diagonal length of the indentation mark in order to avoid any mutual influence of the indentations. In certain cases, crystals split into two along the cleavage plane or crystal surface shattered for loads greater than 50 gram. Thus for each sample several tests were carried out for different loads and average value of the diagonal length of the indentation mark corresponding to each load was used in estimating micro hardness. The hardness number Hv of the crystal was calculated using equation 6.1

Variations of micro hardness with load for the grown samples are shown in the tables 6.1 & 6.2 and in figures 6.2 & 6.3 respectively.
Table 6.1  Applied load and microhardness values for YOx, YBaOx, YCuOx and YBaCuOx crystals

<table>
<thead>
<tr>
<th></th>
<th>YOx</th>
<th>YBaOx</th>
<th>YCuOx</th>
<th>YBaCuOx</th>
</tr>
</thead>
<tbody>
<tr>
<td>Load</td>
<td>H_v (Kg/mm²)</td>
<td>Load (gm)</td>
<td>H_v (Kg/mm²)</td>
<td>Load (gm)</td>
</tr>
<tr>
<td>5</td>
<td>9.0527</td>
<td>5</td>
<td>6.4200</td>
<td>5</td>
</tr>
<tr>
<td>10</td>
<td>12.8393</td>
<td>10</td>
<td>11.0300</td>
<td>10</td>
</tr>
<tr>
<td>50</td>
<td>24.1160</td>
<td>50</td>
<td>21.9000</td>
<td>50</td>
</tr>
</tbody>
</table>

Fig.6.2  Load P vs. H_v graph for YOx, YBaOx, YCuOx and YBaCuOx crystals
Table 6.2  Applied load and microhardness values for PrBaCuOx, NdBaCuOx, GdBaCuOx and DyBaCuOx crystals.

<table>
<thead>
<tr>
<th>PrBaCuOx</th>
<th>NdBaCuOx</th>
<th>GdBaCuOx</th>
<th>DyBaCuOx</th>
</tr>
</thead>
<tbody>
<tr>
<td>Load (gm)</td>
<td>Hv (Kg/mm²)</td>
<td>Load (gm)</td>
<td>Hv (Kg/mm²)</td>
</tr>
<tr>
<td>5</td>
<td>5.7940</td>
<td>5</td>
<td>5.5150</td>
</tr>
<tr>
<td>10</td>
<td>10.5100</td>
<td>10</td>
<td>10.0270</td>
</tr>
<tr>
<td>50</td>
<td>20.6500</td>
<td>50</td>
<td>20.0475</td>
</tr>
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Fig.6.3  Load P versus Hv graph for PrBaCuOx, NdBaCuOx, GdBaCuOx and DyBaCuOx
The graphs of log P against log d (Fig 6.4 & 6.5) for each sample show two distinct lines representing low load region (LLR) and high load region (HLR). The slopes of the straight lines in the LLR and HLR respectively are listed in table 6.3.

**Fig. 6.4** Plot of log P vs. log d for YOx, YBaOx, YCuOx and YBaCuOx crystals
Fig. 6.5  Plot of log P vs. log d for PrBaCuOx, NdBaCuOx, GdBaCuOx and DyBaCuOx

Table 6.3  Mayer indices n₁ (LLR) & n₂ (HLR) for the indentations on the grown samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>LLR n₁</th>
<th>HLR n₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>YOx</td>
<td>4.36162</td>
<td>2.0222</td>
</tr>
<tr>
<td>YBaOx</td>
<td>7.5101</td>
<td>2.0060</td>
</tr>
<tr>
<td>YCuOx</td>
<td>7.3271</td>
<td>2.0609</td>
</tr>
<tr>
<td>YBaCuOx</td>
<td>6.0143</td>
<td>2.369</td>
</tr>
<tr>
<td>PrBaCuOx</td>
<td>9.1027</td>
<td>2.0780</td>
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<tr>
<td>NdBaCuOx</td>
<td>9.3070</td>
<td>2.1160</td>
</tr>
<tr>
<td>GdBaCuOx</td>
<td>9.5207</td>
<td>2.1538</td>
</tr>
<tr>
<td>DyBaCuOx</td>
<td>11.2734</td>
<td>2.1772</td>
</tr>
</tbody>
</table>
The work hardening coefficients, $n_1$ (LLR) and $n_2$ (HLR) from the slopes of $\log P$ vs. $\log d$ graph using least square fit method. The values of $n_1$ and $n_2$ were found to be greater than 2. According to Onitsch’s theory, if $n$ is greater than 2, the materials are said to be soft ones. He also found that microhardness increases with increasing load when $n$ is greater than 2. The increase in $H_v$ for increasing load, $P$, observed in the present study is in good agreement with the theoretical prediction and rare earth oxalate crystals grown in the present study fall in the category of soft materials.

### 6.4 DISCUSSION ON MICROHARDNESS STUDIES

The exponent $n_1$ is larger than 2.0 and non-uniform in LLR for all the indentations. This implies fully softened states least for YOx and maximum for DyBaCuOx crystal. Kick’s law ($n=2$) is not true in this region. Here hardness number depends on the applied load. Variation of microhardness with load can be qualitatively explained on the basis of depth of penetration of the indenter. For small loads, on a few surface layers are penetrated by the indenter. The measured hardness is the characteristics of these layers only and $H_v$ increases rapidly with load in this region. With increase in load, the overall effect is due to surface as well as inner layers of the specimen. In certain samples, it occasionally happens that the mechanical strain exerted by the indenter is sufficient to separate
the layers and produce a cleavage. In these cases, measurements are not possible.

Microhardness of the rare earth oxalates is found to be less than that of the similar salts of calcium. Compounds of heavier metals are softer; especially sulphates, carbonates and phosphates are relatively softer than oxides or sulphides. The Moh’s hardness $H$ is obtained from the Vickers hardness $H_v$ using the conversion formula

$$H = 0.675(H_v)^{1/3} \quad \ldots \ldots \ldots \ldots (6.3)$$

From the present study, maximum hardness of the grown samples can withstand without breaking in Moh’s scale are approximately 1.951, 1.888, 1.930, 1.852, 1.852, 1.833, 1.816 and 1.869 for $YOx$, $YBaOx$, $YCuOx$, $YBaCuOx$, $PrBaCuOx$, $NdBaCuOx$, $GdBaCuOx$ and $DyBaCuOx$ respectively.

Considering Meyer’s equation $P = a d^n$ to be valid, a straight-line graph is expected for log $P$ vs. log $d$. But in the present case, instead of getting a single straight line, two straight lines with different slopes are obtained as shown in Figures 6.3 & 6.4. Buckle discussed the probable reason for such discrepancies. When disturbed specimens are indented with medium loads, the structural factors will distort the basic graph of $H_v$ versus
P and also \( \log P \) versus \( \log d \). In the present study two parallel lines connected by a curve is obtained for \( \log P \) versus \( \log d \) curve. Similar observations were reported by Pandya et al\textsuperscript{12}.

### 6.5 CONCLUSION

The mechanical strength of the grown crystals was determined by measuring the variation of microhardness with load. Microhardness increased with load in all cases while crystals grown showed poor mechanical resistance. Cracks start propagating from the indentation mark when loaded beyond 50 grams. From microhardness measurements it is concluded that the microhardness of the grown rare earth mixed oxalate crystals were found to decrease when both Barium and Copper incorporated into the crystals. This may be due to the lowering of the bond strength when Copper and Barium are added.
6.6 REFERENCES


