CHAPTER 3

MICROHARDNESS INDENTATION SIZE EFFECT STUDIES IN 60B₂O₃-(40-x)PbO-xMCl₂, 50B₂O₃-(50-x)PbO-xMCl₂ (M = Pb, Cd) GLASSES

3.1 Introduction

Microhardness is an important parameter often used to define the mechanical properties of a material on a microscopic scale. Measurement of hardness using a diamond pyramid has long been a practical quality control tool for industry. In a diamond pyramid microhardness tester, a diamond indentor is impressed on a surface at a known load for a known period of time. The area of indentation remaining after removal of the diamond is calculated from the width of the impression of the indentor. The applied load divided by area of the indentation is defined as the hardness (H). Accurate measurements of the hardness of brittle materials have been difficult due to the dependence of hardness on load. This presents a problem to investigators because in the load dependent region making comparison between hardness of materials is difficult.

Hardness is a measure of the resistance of a material to be penetrated and eroded by sharp projections of other materials. Hardness of any material is the result of a complex process of deformation during indentation, the nature of which is more cryptic in the case of glasses because of the limited knowledge of the glass structure. During the process of indentation the material undergoes both compression and shear resulting in the observed deformation, which comprises elastic deformation, flow and densification. Microhardness is the resistance of network against elastic and plastic deformation as well as against compression.
Among the large number of techniques available for hardness measurement,\textsuperscript{2,7} the widely accepted technique of measurement for most materials including glasses is the diamond micro-indenter technique. The shape of the diamond indenter in microhardness testing can be square pyramid (Vickers) or elongated pyramid (Knop). The main advantages of pyramidal indenters\textsuperscript{8} are (1) geometrical similarity of indentation and also hardness values are independent of applied load when loads are larger than 0.5N, (2) the possibility of testing hardness for small loads, (3) the possibility of testing hardness of small areas as well as thin sheets and surface layers, (4) covering a large range of hardness values. Vickers (square pyramid) indentation method is best suitable for hardness measurements in glasses and other brittle materials, because the contact pressure for a pyramid indenters are independent of the indent size and the indentation pattern maintains square geometry even after the onset of cracking. The size of the indentation mark is generally of the order of a few microns under 5 to 1000 g loads.

The pyramidal indenter in microhardness testing gives geometrically similar indentations and the shape of indentation does not vary with load. According to the principle of geometrical similarity, the large indentation is the magnified picture of small indentation, hence the measured hardness should be independent of applied load.\textsuperscript{1} But in microhardness indentation testing measured hardness value depend of on the applied load, which is known as indentation size effect (ISE). It is experimentally well established that apparent hardness measured in a low load range decreases\textsuperscript{9-11} or increases\textsuperscript{12-14} with increase in applied load. According to Gong and Li,\textsuperscript{15} the former is called indentation size effect (ISE) and the latter is called reverse indentation size effect (RISE). ISE is traditionally described through the application of Mayer's law.\textsuperscript{16}

\begin{equation}
P = Ad^n
\end{equation}
where \( P \) is the indentation test load and \( d \) is the resulting indentation size. \( A \) and \( n \) are descriptive parameters derived from the curve fitting of the experimental results. The value of \( n \) is expected to be 2 in the absence of ISE.\(^{11} \) The power law exponent \( n \) between 1 and 2 shows that lower indentation test loads results in higher apparent microhardness.\(^{11} \) For virtually most materials, the power exponent ‘\( n \)’ is experimentally observed to be between 1 and 2. Although the Mayer law has been well proved suitable for representing the experimental data, neither an explanation of the physical meaning of the power law exponent nor the cause of the indentation size effect has been satisfactorily explained.\(^7 \)

Hays and Kandall\(^17 \) have analysed the indentation size effect (ISE) observed on a number of metals, using Knoop microhardness tester. According to these authors, the experimentally measured indentation size is not directly related to applied indentation load \( P \) but to an effective indentation test load defined as \((P-W)\) where \( W \) is the minimum indentation test load, below which plastic deformation does not initiate, but only elastic deformation occurs. Hays and Kandall\(^17 \) modified the relationship between indentation test load and indentation size as

\[
(P-W) = Kd^n
\]

were \( K \) is a constant. Li and Bradt\(^11 \) applied equation (2) to single crystals of TiO\(_2\) and SnO\(_2\) and showed that the magnitude of the load required to initiate plastic flow is surprisingly large and some times greater than the applied indentation test loads. These studies also showed that, there are several inconsistencies in the Hays and Kandall\(^17 \) approach to explain ISE. Accordingly Li and Bradt\(^11 \) formulated the proportional specimen resistance model (PSR) to provide a satisfactory explanation to the ISE. In this model Li and Bradt\(^11 \) assumed that the test specimen resistance \((P)\) is not a constant as proposed by Hays and Kandall but it is directly proportional to indentation size \((d)\). The proportional specimen resistance and indentation size are related by
\[ P_r = a_1d \]  

(3)

were \( a_1 \) is a constant related to the proportional resistance of the test specimen.

The effective indentation load and the indentation size are related as

\[ P - P_r = a_2d^2 \]  

(4)

were \( a_2 \) is a constant related to the load independent hardness or true hardness.

Substituting equation (3) in equation (4),

\[ P = a_1d + a_2d^2 \]  

(5)

Equation (5) can be transformed into

\[ \frac{P}{d} = a_1 + a_2d \]  

(6)

If the PSR model is indeed appropriate, a plot of \( \frac{P}{d} \) vs \( d \) should yield a straight line.

Gong et al\textsuperscript{18,19} studied the PSR model for a number of samples and for a wide range of applied loads. These authors found that \( P/d \) vs \( d \) plots to be non-linear implying that equation (5) does not give an accurate description of ISE, when relatively wider ranges of applied loads are considered. These authors proposed an empirical equation

\[ P = a_0 + a_1d + a_2d^2 \]  

(7)

where \( a_0, a_1 \) and \( a_2 \) are constants. Gong et al\textsuperscript{18,19} applied equation (7) to a number of ceramic samples and showed that experimental results can be correlated by the polynomial equation (7).

Recently Gong and Li,\textsuperscript{15} based on energy balance consideration, and incorporating the possible experimental errors in conventional hardness testing derived the semi-empirical equation (7) to estimate the true hardness of
the test specimen independent of the indenter geometry as well as the indentation size. The validity of this semi-empirical equation was examined using previously published experimental data, in which apparent hardness increased with decrease in load. Gang and Li\textsuperscript{15} proposed that the same equation can be used to evaluate the true hardness value, when apparent hardness value increases with increase in indentation size known as reverse indentation size effect (RISE). To examine ISE or RISE critically, it is necessary to perform an extensive set of experimental microhardness measurements on one material or related materials. Glasses can be used to examine ISE critically because glasses have certain advantages over their crystalline counter parts. Glasses are isotropic and avoid the problems associated with the grain boundaries in polycrystalline materials. Also, there is a possibility of continuously varying the glass composition.

The purpose of the present work was to study the indentation size effect based on the energy balance considerations proposed by Gang and Li\textsuperscript{15} on the glass samples 60B\textsubscript{2}O\textsubscript{3}-(40-x)PbO-xMCl\textsubscript{2} and 50B\textsubscript{2}O\textsubscript{3}-(50-x)PbO-xMCl\textsubscript{2} (M = Cd or Pb) for different compositions (x = 10, 12.5, 15, 17.5 and 20 mole percentage). The load independent microhardness values of these glass samples were calculated using the empirical relation given by Gong and Li\textsuperscript{15}. The calculated true hardness values were compared with experimentally determined microhardness values. The variations of true hardness values with addition of PbCl\textsubscript{2} or CdCl\textsubscript{2} in the glass systems are discussed.

3.2 Experimental

Four sets of glass samples 60B\textsubscript{2}O\textsubscript{3}-(40-x)PbO-xPbCl\textsubscript{2}, 50B\textsubscript{2}O\textsubscript{3}-(50-x)PbO-xPbCl\textsubscript{2}, 60B\textsubscript{2}O\textsubscript{3}-(40-x) PbO-xCdCl\textsubscript{2}, and 50B\textsubscript{2}O\textsubscript{3}-(50-x)PbO-xCdCl\textsubscript{2} of different compositions (x = 10, 12.5, 15, 17.5, 20) and with sample codes given in (table 3.1 and 3.2) were prepared as described in section 2, chapter 2 of this thesis.
The micro hardness of the glass samples was measured by using Vickers indentation method. A hardness tester (Leitz Miniload L) fitted with a diamond pyramidal indenter and attached to an incident light microscope (Leitz Matalux 3) was used for the study. The Vickers diamond indenter was applied perpendicular to the glass samples at different sites having no surface defects visible under the microscope. The schematic diagram of the Vickers diamond pyramid indenter and an indentation mark are shown in the figure 3.1a and 3.1b respectively.

![Figure 3.1. Schematic diagram of the (a) Vickers diamond pyramid indenter and (b) an indentation mark](image)

The base of the Vickers pyramidal indenter is a square, and the longitudinal and the transverse diagonals are in the ratio 7:1. The diagonal of the impression was measured with a calibrated ocular 500-fold magnification. The load $P$ was varied from 5 g to 500 g and the time of indentation was kept constant at 30 seconds for all measurements. The distance between any two indentations was kept more than five times the diagonal length of the indentation, to avoid mutual influence of the indentations. For each load, ten trials of indentation were carried out and the average value of the diagonal length of indentation marks was determined. The indentations
were carried out at room temperature. The diagonal length measurement was made on selected impressions having perfect square shape.

3.3 Theory

The hardness number, $H$, is defined as the applied load ($P$) divided by the contact area ($A$), between indenter and the sample

$$H = \frac{P}{A}$$

In the case of Vickers hardness tester, a square based pyramidal indenter is used and the contact area is

$$A = \frac{d^2}{2 \sin \frac{\theta}{2}}$$

where $\theta = 136^\circ$ is the angle between the opposite faces of the diamond pyramid indenter and $d$ is the average diagonal length of the impression. Vickers microhardness number $H_\nu$ for each load is then given by the relation

$$H_\nu = 1.8544 \frac{P}{d^2} \text{ (Kg/mm$^2$)} \quad (8)$$

where $P$ is the applied load in Kg and $d$ is the diagonal length of the indentation in mm.

Equation (8) can be modified as

$$pd = \frac{H_\nu d^3}{k} = \beta H_\nu d^3 \quad \text{where } k = 1.8544 \text{ and } \beta = 1/1.8544 \quad (9)$$

The indentation size ($d$) is directly proportional to the indentation depth ($h$) if the experimental errors related to the smallness of the indentation are neglected. The left hand side of equation (9) is a measure of the work done by the applied load during indentation and right hand side is a measure of the energy used to produce the permanent deformation. If the applied force is
completely transformed to the energy used for producing permanent deformation, a constant value of hardness can be expected. But, formation of micro-cracks, migration of grain boundaries, deformation of intrinsic pores, etc can cause extra dissipation of energy. The energy dissipated by all these phenomena may be considered to be proportional to the area of the indentation mark, $d^2$.

Thus equation (9) can be modified as

$$Pd = \alpha d^2 + \beta H_d d^3$$  \hspace{1cm} (10)

where $\alpha$ is a constant dependent on the surface energy of test material and $H_d$ is the true hardness.

Dividing equation (10) by $d$ gives equation (5) given by Li and Bradt for the PSR model.

According to Gong and Li, the main reason for the deviation of experimental data from the equation (8) or (5) is that these equations do not incorporate the experimental errors arising from elastic recovery of indentation, optical resolution of the objective of the lens used, the sensitivity of the load cell (an apparatus which measures the load and diamond indentation simultaneously) etc. If $P_0$ is the true value of applied load and $d_0$ the resulting indentation size, then the equation

$$P_0 = \alpha d_0 + \beta H_d d_0^2$$  \hspace{1cm} (11)

would represent the experimental data.

Incorporating the experimental errors, which inevitably get involved in conventional hardness testing, into the true value of load $P_0$ and resulting indentation diagonal length ($d_0$), we have

$$P' = P + \eta$$  \hspace{1cm} (12a)
where \( \eta \) and \( \delta \) are constants dependent on the test material, the test machine and the test conditions, and \( P \) and \( d \) are applied load and experimentally determined indentation length, respectively. Substituting equations (12a) and (12b) into equation (11),

\[
P = (\beta H \delta^2 + \alpha \delta - \eta) + (2H \delta + \alpha)d + \beta H \delta^2
\]

Above equation can be written as

\[
P = a_0 + a_1 d + a_2 d^2
\]

where

\[
a_0 = \beta H \delta^2 + \alpha \delta - \eta
\]

\[
a_1 = 2H \delta + \alpha
\]

\[
a_2 = \beta H
\]

Equation (14) is of the same form of empirical equation (7) proposed by Gong et al. The value of \( a_2 \) depends only on the true hardness. \( a_0 \) and \( a_1 \) are function of true hardness, surface energy and experimental errors. Equation (14c) can be used to calculate the true hardness (\( H_T \)).

Substituting equation (14) in equation (8)

\[
H_T = 1.8544\left(\frac{a_0 + a_1 d + a_2 d^2}{d^2}\right) = 1.8544\left(\frac{a_0}{d^2} + \frac{a_1}{d}\right) + H_T
\]

or

\[
\Delta H = H_T - H_T = 1.8544\left(\frac{a_0}{d^2} + \frac{a_1}{d}\right)
\]

where \( H_T \) is the apparent Vickers hardness, \( H_T \) is the true hardness and \( \Delta H \) is the difference between apparent hardness and true hardness. Equation (16) reveals that a difference (\( \Delta H \)) exists between the apparent hardness (\( H_T \))
defined by equation (8) and true hardness ($H_T$). In the case of reverse indentation size effect (RISE) in which apparent hardness increases with increase in indentation size, $\Delta H$ is negative and increases with increase in $d$. When measurements are conducted at relatively higher level of applied load, $\Delta H$ approaches to zero, the apparent hardness value becomes equal to the true hardness value and can also be explained using equation (16).

3.4 Results and Discussion

Plots of variation of microhardness number of the glass samples 60B$_2$O$_3$-(40-x)PbO-xPbCl$_2$, 60B$_2$O$_3$-(40-x)PbO-xCdCl$_2$, 50B$_2$O$_3$-(50-x)PbO-xPbCl$_2$ and 50B$_2$O$_3$-(50-x)PbO-xCdCl$_2$ with applied load are shown in figures 3.2 to 3.5.

![Figure 3.2. Variation of microhardness ($H_m$) with load (P) of 60B$_2$O$_3$-(40-x) PbO-xPbCl$_2$ glasses of different composition](image-url)
Figure 3.3. Variation of microhardness ($H_v$) with load ($P$) of $50B_2O_3-(50-x)\ PbO-xPbCl_2$ glasses of different composition.

Figure 3.4. Variation of microhardness ($H_v$) with load ($P$) of $60B_2O_3-(40-x)\ PbO-xCdCl_2$ glasses of different composition.
Figure 3.5. Variation of microhardness ($H_v$) with load (P) of $50B_2O_3-(50-x)$ PbO-$xCdCl_2$ glasses of different composition

Typical photograph of indentation mark at a load 100g is shown in figure 3.6.

From the figures 3.2 to 3.5 it can be seen that the hardness number increases rapidly at lower values of the load, then increase at a slower rate and finally attains practically a constant value. In Vickers hardness tester, the diamond indenter is a square pyramid and the shape of the indentation does not vary with load. According to the principle of geometrical similarity, a large indentation is a magnified picture of a small indentation.
Figure 3.6. Sample indentation mark at a load of 100 g

Hence hardness should be independent of the load\textsuperscript{1}. But, experimentally measured microhardness number in the low load region decreases (ISE) or increases (RISE) with increase in load. This indentation load or size effect on the microhardness, was attributed to a verity of phenomenon like work hardening during indentation,\textsuperscript{2} load to initiate plastic deformation,\textsuperscript{17} the indentation elastic recovery,\textsuperscript{20} plastic deformation band spacing\textsuperscript{22} and effect of distorted zone\textsuperscript{12,13} etc. Surface polishing of the sample prior to indentation can also be a cause of ISE, because surface polishing introduces plastic deformation and cracks into the material adjacent to the surface.\textsuperscript{18} But the exact cause of the indentation load or size effect has not satisfactorily been determined.\textsuperscript{11}

At small loads, the indenter may penetrate only to the vicinity of the surface. With increase in load, penetration depth increases. Beyond a certain limit, the indenter penetrates beyond the surface and the bulk density of inner zone may be different from the surface density. For all the glass samples in the present study \{60B\textsubscript{2}O\textsubscript{3}-(40-x)PbO-xPbCl\textsubscript{2}, 60B\textsubscript{2}O\textsubscript{3}-(40-x)PbO-xCdCl\textsubscript{2}, 50B\textsubscript{2}O\textsubscript{3}-(50-x)PbO-xPbCl\textsubscript{2} and 50B\textsubscript{2}O\textsubscript{3}-(50-x)PbO-xCdCl\textsubscript{2}\}, \(H_v\) was found to be practically independent of the load above 100g. Hennicke and Vaupel\textsuperscript{23} reported that for silica glass samples the hardness was load independent above a critical load but load dependent below that load. The critical load was approximately 0.8N for silica glasses\textsuperscript{23}.
The applied load is related to the diagonal of the impression through Mayer's relation [equation (1)]. The Mayer index $n = 2$ for all indentations, and for all geometrically similar impressions, under the condition that the measured hardness is truly independent of the load. However, according to Oritsch and Grodzinski, $n < 2$ in the region where microhardness number $H_v$ decrease with increase in the load, and $n > 2$ if $H_v$ increases with increase in load. In the present investigation, the Mayer index $n$ was determined from the slope of log $d$ vs log $P$ graph using least squares fit method (Figures 3.7 to 3.10). For all the glass samples, plots of log $d$ vs log $P$ were found to be straight lines below and above a load of 100g. In the lower load region, the value of $n$ was found to be larger than the theoretical value of 2 for the glass systems $60B_2O_3-(40-x)PbO-xPbCl_2$, $50B_2O_3-(50-x)PbO-xPbCl_2$, $60B_2O_3-(40-x)PbO-xCdCl_2$, $50B_2O_3-(50-x)PbO-xCdCl_2$ (table 3.1 and 3.2), and $H_v$ increased with increase in the load. In the higher load region, the value of $n$ was approximately equal to the theoretical value of 2 (table 3.1 and table 3.2), indicating hardness number was independent of the applied load.

![Figure 3.7. Variation of log d vs log P of 60B_2O_3-(40-x)PbO-xPbCl_2 glasses of different composition](image-url)
Figure 3.8. Variation of log d vs log P of 50B$_2$O$_3$-(50-x)PbO-xPbCl$_2$ glasses of different composition

Figure 3.9. Variation of log d vs log P of 60B$_2$O$_3$-(40-x)PbO-xCdCl$_2$ glasses of different composition
Figure 3.10. Variation of $\log d$ vs $\log P$ of $50B_2O_3-(50-x)PbO-xCdCl_2$ glasses of different composition

Table 3.1

Sample code, glass composition and Mayer index of the glass samples $60B_2O_3-(40-x) \text{PbO}-x\text{PbCl}_2$ and $50B_2O_3-(50-x)\text{PbO}-x\text{PbCl}_2$ of different composition.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Glass composition</th>
<th>Mayer index (n)</th>
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</thead>
<tbody>
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<td></td>
<td></td>
<td>Below 100 g</td>
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<tr>
<td>BPP1</td>
<td>$60B_2O_3-30PbO-10PbCl_2$</td>
<td>3.14</td>
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Table 3.2

Sample code, glass composition and Mayer index of the glass samples $60B_2O_3-(40-x)PbO-xCdCl_2$ and $50B_2O_3-(50-x)PbO-xCdCl_2$ of different composition.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Glass composition</th>
<th>Mayer index(n)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Below 100 g</td>
<td>Above 100 g</td>
</tr>
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</table>

Typical plots of indentation diagonal length (d) vs applied load (P) for selected glass samples (to save space, only typical plots are given) in the present study are shown in Figures 3.11 to 3.14. The solid lines in the plots are obtained by polynomial regression according to equation (14). From the Figures 3.11 to 3.14, it is clear that equation (14) can be used to represent the experimental data. The best-fit parameters ($a_0$, $a_1$ and $a_2$) included in the equation (14) for all the 20 glass samples studied are given in the table 3.3 and 3.4. The true value of hardness $H_T$ was calculated from the coefficient $a_2$ using the equation 14(c).
Figure 3.11. Plot of indentation size as a function of applied load for 60B_2O_3-\((40-x)\)PbO-\(x\)PbCl_2 glasses of different composition.

Figure 3.12. Plot of indentation size as a function of applied load for 50B_2O_3-\((50-x)\)PbO-\(x\)PbCl_2 glasses of different composition.
Figure 3.13. Plot of indentation size as a function of applied load for $60\text{B}_2\text{O}_3-(40-\text{x})\text{PbO}-\text{xCdCl}_2$ glasses of different composition.

Figure 3.14. Plot of indentation size as a function of applied load for $50\text{B}_2\text{O}_3-(50-\text{x})\text{PbO}-\text{xCdCl}_2$ glasses of different composition.
Using the best-fit values of the parameter $a_0$ and $a_1$ listed in the table, the difference between the values of the apparent hardness and true hardness $\Delta H = H - H_T$ was calculated as a function of indentation size according to equation (16). Figures 3.15 to 3.18 show the typical plots of theoretically calculated $\Delta H = H - H_T$ as a function of applied load. In the same plots, the difference between experimentally measured hardness value ($H_\text{m}$) and true hardness ($H_T$) is also shown as a function of applied load. It can be seen that in both the cases $\Delta H$ increases with the applied load. When the applied load increases to a limiting value the value of $\Delta H$ becomes so small that apparent hardness $H_\text{m}$ become equal to the true hardness ($H_T$).

**Figure 3.15.** Plot of calculated $\Delta H$ and measured $\Delta H$ as a function of applied load for $60B_2O_3-(40-x)PbO-xPbCl_2$ glasses of different composition.
Figure 3.16. Plot of calculated $\Delta H$ and measured $\Delta H$ as a function of applied load for $50B_2O_3-(50-x)PbO-xPbCl_2$ glasses of different composition.

Figure 3.17. Plot of calculated $\Delta H$ and measured $\Delta H$ as a function of applied load for $60B_2O_3-(40-x)PbO-xCdCl_2$ glasses of different composition.
Figure 3.18. Plot of calculated $\Delta H$ and measured $\Delta H$ as a function of applied load for 50B$_2$O$_3$-(50-x)PbO-xCdCl$_2$ glasses of different composition.

The value of the true microhardness $H_T$ and experimentally determined microhardness $H_e$ for an applied load of 200g, for all the glass samples in the present study are given in the table 3.3 and 3.4. At loads $<$ 200 g, hardness number was load dependent and at higher loads micro cracks that would affect the measured hardness value appeared. It was found that value of $H_e$ was larger than $H_T$ in all most all cases (table 3.3 and 3.4). The test specimen used in the present study were polished mechanically. Surface polishing removes material mechanically and introduces residual stresses on the surfaces of test specimen$^{26}$ which in turn produces plastic deformation and cracks in the region adjacent to the surface.$^{18,19}$ Mechanically polished surface would be plastically deformed and would be in a state of compression.$^{27}$ In microhardness testing, a sharp indenter plastically deforms small volume of the material adjacent to the surface. Although a qualitative analysis relating to the effect of plastically deformed surface on the hardness is still lacking,$^{18}$ there are reasons to believe that the experimentally observed microhardness...
values \( H_v \) are different from the true microhardness value \( H_T \) (table 3.3 and 3.4). The true microhardness value \( H_T \) is independent of the indentation size and is free from the possible experimental errors in microhardness testing.

**Table 3.3**

Sample code, best fit parameters in equation (14), true hardness, and measured hardness for a load 200gm of samples 60B_2O_3-(40-x) PbO-xPbCl_2 and 50B_2O_3-(50-x) PbO-xPbCl_2 of different composition.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Best fit parameters in Equation(14)</th>
<th>Microhardness values (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( a_0 )</td>
<td>( a_1 \times 10^3 ) ( J/m^2 )</td>
</tr>
<tr>
<td>BPP1</td>
<td>-0.421</td>
<td>3.06</td>
</tr>
<tr>
<td>BPP2</td>
<td>-0.302</td>
<td>9.64</td>
</tr>
<tr>
<td>BPP3</td>
<td>-0.641</td>
<td>31.17</td>
</tr>
<tr>
<td>BPP4</td>
<td>-0.615</td>
<td>27.61</td>
</tr>
<tr>
<td>BPP5</td>
<td>-0.752</td>
<td>32.09</td>
</tr>
<tr>
<td>BPP6</td>
<td>-0.688</td>
<td>16.88</td>
</tr>
<tr>
<td>BPP7</td>
<td>-1.183</td>
<td>43.18</td>
</tr>
<tr>
<td>BPP8</td>
<td>-0.760</td>
<td>26.413</td>
</tr>
<tr>
<td>BPP9</td>
<td>-0.813</td>
<td>28.375</td>
</tr>
<tr>
<td>BPP10</td>
<td>-1.223</td>
<td>46.316</td>
</tr>
</tbody>
</table>
Table 3.4

Sample code, best fit parameters in equation (14), True hardness, and measured hardness for a load 200gm of 60B₂O₃-(40-x)PbO-xCdCl₂ and 50B₂O₃-(50-x)PbO-xCdCl₂ of different composition.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Best fit parameters in Equation(14)</th>
<th>Microhardness values (GPa)</th>
<th>Measured hardness at 200g load(Hₜ)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$a_0$(J/m)</td>
<td>$a_1$x10³(J/m³)</td>
<td>$a_2$x10⁶(J/m³)</td>
</tr>
<tr>
<td>BPC1</td>
<td>-0.504</td>
<td>16.75</td>
<td>2436.32</td>
</tr>
<tr>
<td>BPC2</td>
<td>-0.527</td>
<td>19.33</td>
<td>2269.33</td>
</tr>
<tr>
<td>BPC3</td>
<td>-0.598</td>
<td>29.77</td>
<td>1852.02</td>
</tr>
<tr>
<td>BPC4</td>
<td>-0.601</td>
<td>34.86</td>
<td>1839.84</td>
</tr>
<tr>
<td>BPC5</td>
<td>-0.476</td>
<td>32.97</td>
<td>1731.17</td>
</tr>
<tr>
<td>BPC6</td>
<td>-0.543</td>
<td>19.91</td>
<td>2214.64</td>
</tr>
<tr>
<td>BPC7</td>
<td>-0.576</td>
<td>28.25</td>
<td>2131.8</td>
</tr>
<tr>
<td>BPC8</td>
<td>-0.577</td>
<td>29.84</td>
<td>2041.57</td>
</tr>
<tr>
<td>BPC9</td>
<td>-0.435</td>
<td>19.73</td>
<td>1914.32</td>
</tr>
<tr>
<td>BPC10</td>
<td>-0.657</td>
<td>38.59</td>
<td>1719.44</td>
</tr>
</tbody>
</table>

Plots of true microhardness number ($H_T$) vs mole percentage of PbCl₂ or CdCl₂ contained in the glass samples are shown in Figure 3.19. As seen from the graph, the value of true microhardness ($H_T$) decreases as the mole percentage of PbCl₂ or CdCl₂ is increased.
The observed decrease in true microhardness value ($H_T$) with increase in mole percentage of PbCl$_2$ or CdCl$_2$ (Figure 3.19) can be explained on the basis of direct substitution of PbCl$_2$ or CdCl$_2$ for PbO. The change from triangular BO$_3$ to tetrahedral BO$_4$ groups with decreasing mole percentage of B$_2$O$_3$ is the major feature of the structural change in binary$^{28}$ and ternary borate glasses.$^{29}$ In addition, the non-bridging oxygen (NBO) in borate glasses plays an important role in deciding the structural changes with composition of glasses. The presence of BO$_4$ tetrahedra with bridging oxygen in the glass structure will cause maximum connectivity of the glass network giving more rigidity to the structure and resulting in an increase in microhardness.

Doweidar et al$^{30}$ reported the study of microhardness of ZnO-PbO-B$_2$O$_3$ glasses and observed that a sudden decrease of microhardness ($H_T$) number occurred between 60 and 62.5 mole percentage of (ZnO + PbO). The
decrease in microhardness was attributed to the expansion of glass network due to the formation of non-bridging oxygen.

It is generally accepted that the molecular building block of vitreous B_2O_3 is planar BO_3 triangles, which are linked at the corners to form two-dimensional network. The addition of PbO to the B_2O_3 network converts BO_3 units into BO_4 tetrahedra until one half of the boron-oxygen units are tetrahedra, with Pb^{2+} ions acting as charge compensators for negatively charged BO_4^- units. Beyond this concentration, the structure begins to depolimerized and non-bridging oxygens (NBO) are formed in the network.

For a constant concentration of B_2O_3, when PbCl_2 is substituted for PbO in B_2O_3-PbO-PbCl_2 glass system, a local change in the structure is expected. Substitution of PbCl_2 for PbO results in direct replacement of one O^{2-} ion for two Cl^- ions. As more and more PbCl_2 is substituted for PbO, the Cl^- ion concentration in the network increases. In addition, the ionic radius of Cl^- ions (0.181nm) is larger than that of O^- ions (0.132nm). As a result the glass network becomes systematically weakened and a more open network is formed, in order to accommodate of the excess chlorine ions.34

FTIR studies of the glass samples in the present study are given in the chapter 2 of this thesis. It was seen that the fraction of tetrahedrally coordinated boron atoms (N_4) decreased as PbCl_2 or CdCl_2 was substituted for PbO in 60B_2O_3-(40-x)PbO-xMCl_2 and 50B_2O_3-(50-x)PbO-xMCl_2 (M = Pb,Cd) glasses. Tetrahedrally coordinated boron atoms (N_4) with bridging oxygen in the glass structure give maximum connectivity to borate glass network. Decrease in N_4 with the addition of PbCl_2 or CdCl_2 for PbO showed that the glass structure in the present study became systematically weakened. Development of an open structure through the formation of non-bridging chlorine or non-bridging oxygen would, there for lower the microhardness of the glass samples in the present study.
In order to check whether decrease in microhardness value was due to the excess Cl ions in the network, in the case of 60B₂O₃-(40-x)PbO-xCdCl₂, 50B₂O₃-(50-x)PbO-xCdCl₂ glasses, CdCl₂ was substituted for PbO, in a similar fashion as PbCl₂ was substituted for PbO in 60B₂O₃-(40-x)PbO-xPbCl₂ and 50B₂O₃-(50-x)PbO-xPbCl₂ glasses. In 60B₂O₃-(40-x)PbO-xPbCl₂ and 50B₂O₃-(50-x)PbO-xPbCl₂ glasses when PbCl₂ was substituted for PbO, the total Pb content remained constant in the glass system while the chlorine ion concentration increased. But in 60B₂O₃-(40-x)PbO-xCdCl₂, 50B₂O₃-(50-x)PbO-xCdCl₂ glasses, CdCl₂ was substituted for PbO, the chlorine ion concentration increased in a similar way as in the case of 60B₂O₃-(40-x)PbO-xPbCl₂ and 50B₂O₃-(50-x)PbO-xPbCl₂ glasses, while the Pb content concentration decreased. The variation of true hardness value (H₁) in CdCl₂ substituted glasses show a variation similar to that of PbCl₂ substituted glasses (Figure 3.19) indicating that decrease in microhardness value is due to the expansion of network due to the excess of Cl⁻ ions in the network and not due to the cations (Pb²⁺, Cd²⁺) in the glass structure.

3.5 Conclusion

Vickers microhardness of glasses of the system 60B₂O₃-(40-x) PbO-xMC1₂ and 50B₂O₃-(50-x)PbO-xMC1₂ (M=Cd, Pb) was investigated for 20 different glass compositions. The hardness number showed an increase in its value up to a load of 100 g and then became practically a constant. At smaller loads (< 100g), the hardness increased rapidly. The indentation size effect (ISE) on the microhardness was discussed and the load independent true microhardness values were evaluated. The decrease of true microhardness with increase in mole percentage of PbCl₂ or CdCl₂ was discussed on the basis of expansion of the glass network due to the incorporation of excess of Cl⁻ ions in the network.
References

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