Microhardness study of $(1 - x - y)(\text{B}_2\text{O}_3) - x(\text{Li}_2\text{O}) - y(\text{MCl}_2)$, (M = Cd, Zn) glasses

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Abstract. Results of microhardness measurements on $(1 - x - y)(\text{B}_2\text{O}_3) - x(\text{Li}_2\text{O}) - y(\text{MCl}_2)$, (M = Cd, Zn) glasses, in the applied load range 25–500 g, are presented. The microhardness was found to decrease with increase in load up to 50 g, then it increased and finally attained a practically constant value with increase in load. The effects of composition of the glasses on microhardness are discussed.

Keywords. Borate glasses; microhardness; non-alkali halide glasses.

1. Introduction

Studies on microhardness have been routinely applied to understand the plasticity of crystals (Mott 1956). Hardness is a measure of resistance of a material to being penetrated and eroded by sharp projections of another material. The scratching capability of various minerals is ranked using the Mohs scale of hardness spanning from 1 to 10, 10 being for diamond which is rated the hardest (Varshneya 1994). Most oxide glasses fall between 5 and 7. Various techniques are available for hardness measurement and are adequately described in literature (Mott 1956; Neill 1967). The hardness of a glass is usually expressed in terms of indentation hardness such as Vickers or Knoop hardness. These have been used not only as practical classifiers, but also as means of obtaining information concerning the structure and mechanical properties of glasses. However, there is a question as to whether the indentation size is affected by densification (Hillig 1963; Ernsberger 1968; Neely and Mackenzie 1968) or microplastic flow (Taylor 1950; Marsh 1961, 1964). The static indentation test is the most important type of hardness test and covers a wide range of testing conditions. For Vickers micro indenter, the hardness is expressed as Vickers hardness number (H_v). The H_v of SiO_2 glass is generally quoted (Varshneya 1994) at about 630 kgf/mm² and that of B_2O_3 at about 205 kgf/mm². The addition of alkalis is reported to cause a decrease in the hardness of silica glass and this observation is interpreted as due to a decrease in the connectivity of the structure (Varshneya 1994). But in B_2O_3 glasses the addition of alkalis causes the conversion of BO_3 to four-fold co-ordinated borons thereby increasing the connectivity and the hardness (Varshneya 1994). There are a few reports

on the study of hardness of chalcogenide (Sreeram *et al* 1991) and oxide glasses (Farkhonda *et al* 1979; Bansal and Doremus 1986). The role of Na_2O , K_2O , and BaO on microhardness of lead silicate glass has been studied recently by Shrikhande *et al* (1998). These authors have reported that the microhardness of glass increased at higher concentration of the modifier ions but this effect was more pronounced when the concentration of Na_2O was increased.

The present article reports the results of microhardness study of $(1 - x - y)(\text{B}_2\text{O}_3) - x(\text{Li}_2\text{O}) - y(\text{MCl}_2)$, (M = Cd, Zn) glasses of different compositions. The dependence of microhardness on glass composition and applied load is discussed.

2. Experimental

Fourteen glass samples of different compositions (table 1) with code numbers BZL1 to BZL7 and BCL1 to BCL7 were prepared. Calculated quantities of the chemicals were mixed thoroughly in an agate mortar and heated to 950°C in a porcelain crucible, so that a homogeneously mixed melt was obtained. The samples were made using splat-quenching technique and were annealed at a temperature of about 450°C for 4 h. The grinding and fine polishing of the glass samples was found possible only if the samples were annealed at a temperature above nearly 400°C. The samples were cooled to room temperature and then polished. Glass discs of thickness about 1 mm, and with smooth and parallel faces were obtained. The glass samples were polished using fine grinding powder. Flat glass plates with smooth and parallel surface for the microhardness studies were thus obtained.

The microhardness of the glass samples was measured by using Vickers indentation method. A hardness tester (Leitz Mini load L) fitted with a diamond pyramidal

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Table 1. Glass composition.

No.	Glass composition	Code	No.	Glass composition	Code
1	0.75B ₂ O ₃ -0.20ZnCl ₂ -0.05Li ₂ O	BZL1	1	0.75B ₂ O ₃ -0.20CdCl ₂ -0.05Li ₂ O	BCL1
2	0.70B ₂ O ₃ -0.20ZnCl ₂ -0.10Li ₂ O	BZL2	2	0.70B ₂ O ₃ -0.20CdCl ₂ -0.10Li ₂ O	BCL2
3	0.65B ₂ O ₃ -0.20ZnCl ₂ -0.15Li ₂ O	BZL3	3	0.65B ₂ O ₃ -0.20CdCl ₂ -0.15Li ₂ O	BCL3
4	0.60B ₂ O ₃ -0.20ZnCl ₂ -0.20Li ₂ O	BZL4	4	0.60B ₂ O ₃ -0.20CdCl ₂ -0.20Li ₂ O	BCL4
5	0.75B ₂ O ₃ -0.05ZnCl ₂ -0.20Li ₂ O	BZL5	5	0.75B ₂ O ₃ -0.05CdCl ₂ -0.20Li ₂ O	BCL5
6	0.70B ₂ O ₃ -0.10ZnCl ₂ -0.20Li ₂ O	BZL6	6	0.70B ₂ O ₃ -0.10CdCl ₂ -0.20Li ₂ O	BCL6
7	0.65B ₂ O ₃ -0.15ZnCl ₂ -0.20Li ₂ O	BZL7	7	0.65B ₂ O ₃ -0.15CdCl ₂ -0.20Li ₂ O	BCL7

indenter, attached to an incident light microscope (Leitz Metallucx 3) was used for the study. The Vickers diamond indenter was applied perpendicular to the glass samples on different sites having no surface defects. The load p was varied from 25 to 500 g and the time of indentation was the same (30 sec) for all trials and samples. The distance between any two indentations was more than three times the diagonal of the nearest indentation, to ensure that the indentation is created on a perfect surface. For each glass sample, several trials of indentation with each load were made and the average values of the diagonal lengths of indentation marks were obtained. The diagonal length measurement was strictly made on the selected impressions having similar shape. The Vickers microhardness number H_v at each load was calculated using the relation,

$$H_v = 1.8544 p/d^2 \text{ (kg/mm}^2\text{)},$$

where p is the applied load in kg and d the diagonal length of the indentation in mm.

3. Results and discussion

When an indentation is made in a glass, the glass is elastically compressed initially. Once the elastic limit is reached, the balance of the hydrostatic stress component permanently densifies the glass under the indentation, whereas the balance of the shear component causes the glass to undergo plastic deformation. When the indentation is withdrawn, the elastic portion recovers, i.e. a slight shrinkage of the size of the impression takes place (Varshneya 1994). Hence the hardness number has to be expected to be dependent on applied load. A plot of the microhardness number for the glass samples against the applied load in the present study is shown in figures 1 and 2.

The hardness number shows a decrease up to a load of about 50 g, then it increases with load and finally becomes practically independent of load. On subjecting SiO₂, GeO₂ and B₂O₃ glasses to different pressure transmitting media, Mackenzie (1963) found that densification in these systems increased with time, temperature, pressure and applied shear. He attributed these results to

Figure 1. Variation of microhardness number (H_v) of BCL glasses with load (p). **Figure 2.** Variation of microhardness number (H_v) of BZL glasses with load (p).

the mutual entanglement of parts of the random glassy network. Neely and Mackenzie (1968), and Izumitani and Suzuki (1973) showed that the indentation is due primarily to densification of a volume of glass in the vicinity of the indenter. That in glasses many indentation

effects occur by densification and not by plastic flow was proposed by Ernsberger (1968) also. But the role of microplasticity rather than densification in the indentation hardness of several optical glasses containing large amounts of modifiers is considered to be important by some workers in this field (Farkhonda *et al* 1979). It is the generally approved notion that behaviour of microhardness of glasses might be complex because of the fact that it is an exhibition of a process involving flow, compression, and failure, and not a defined physical property. In the present study the marked change in hardness number for the change in loads from 25 to 100 g may be attributed to the generation of plastic deformation, since a drastic change in density to produce such a pronounced change in microhardness cannot be expected. The somewhat constant hardness values (except for the slight deviation for the samples BZL4 and BZL7) for loads above 100 g might be due to the workhardening of the glasses (Mott 1956).

Kick (Sagayaraj *et al* 1990) proposed an analysis of results on hardness and according to him the relation between applied load, p and indentation length, d is

$$p = K_1 d^n,$$

where K_1 (standard hardness) and n are constants (Sagayaraj *et al* 1990). The value of n represents the capacity of workhardening. Kick postulated a constant value of $n = 2$ for all of the indentors and for all geometrically similar impressions. However, according to Grodzinski (1953) and Onitsch (1950), $n < 2$ in the region where H_v decreases with increase in load. In the present investigation the workhardening coefficient n and K_1 were determined using least squares fit method (figures 5 and 6)

Figure 3. Variation of microhardness number (H_v) with mole % of Li_2O (a) and with mole % of CdCl_2 (b) in BCL glasses.

and n was found to be less than 2 for both the glass systems (table 2) which is in accordance with Grodzinski's concept.

A plot of microhardness number vs mole percentage of Li_2O , and CdCl_2 or ZnCl_2 (figures 3 and 4), shows a considerable increase in microhardness apparently indicative of structural changes in the glasses. The densities of BCL and BZL glasses as a function of the glass composition are shown in figure 7. There is a tendency for the density to increase with increase in the concentration of Li_2O or ZnCl_2 , but the density first decreases and then increases with increasing concentration of CdCl_2 . The change from triangular BO_3 to tetrahedral BO_4 groups

Figure 4. Variation of microhardness number (H_v) with mole % of Li_2O (a) and with mole % of ZnCl_2 (b) in BZL glasses.

Figure 5. Plot of $\log d$ vs $\log p$ of BCL glasses.

Figure 6. Plot of $\log d$ vs $\log p$ of BZL glasses.

Figure 7. Variation of density (ρ) with mole percentage of Li_2O (x) and CdCl_2 or ZnCl_2 (y) in BCL and BZL glasses.

with decreasing B_2O_3 concentration is the major feature of structural change in binary (Greenblatt and Bray 1967) and ternary (Konijnend 1976) borate glasses. Kamitsos *et al* (1990) reported that the absorption envelope of B_2O_3 – Li_2O glass indicate the initial creation of BO_4 tetrahedra containing groups for low concentration of Li_2O , ($0 < \text{Li}_2\text{O} \leq 0.40$) and their subsequent destruction in favour of non bridging oxygen bearing units for higher Li_2O concentration ($\text{Li}_2\text{O} > 0.40$).

The presence of the BO_4 tetrahedra with bridging oxygens in the structure will give more rigidity to the structure, causing maximum connectivity of the glass

Table 2. Workhardening-coefficient (n) for various glass compositions.

Sample code	Workhardening coefficient (n)
BCL1	1.88
BCL2	1.64
BCL3	1.65
BCL4	1.62
BCL5	1.82
BCL6	1.72
BCL7	1.65
BZL1	1.59
BZL2	1.58
BZL3	1.66
BZL4	1.76
BZL5	1.69
BZL6	1.62
BZL7	1.71

network and increase in microhardness. In the case of $x(\text{PbO})-(1-x)(\text{B}_2\text{O}_3)$ glasses (Farkhonda *et al* 1979), it is reported that the microhardness considerably decreased with concentration of PbO indicating structural changes, but no conspicuous correlation between microhardness and concentration of BO_4 groups is stressed. It is also reported (Farkhonda *et al* 1979) that when PbO in lead borate glasses was substituted by small concentration of Na_2O , K_2O , or Li_2O , the density of the glass and microhardness increased substantially, and the increase appears to saturate above a finite concentration of the alkali oxide. This effect was attributed to the consolidation of the glass-forming network when smaller ions substitute for Pb^{2+} . In the present study it was found that the microhardness of both the types of glasses, $(1-x-y)(\text{B}_2\text{O}_3)-x(\text{Li}_2\text{O})-y(\text{CdCl}_2)$, and $(1-x-y)(\text{B}_2\text{O}_3)-x(\text{Li}_2\text{O})-y(\text{ZnCl}_2)$, decreased with increase of load up to 50 g and above a load of 100 g the hardness reached an almost constant value. The workhardening coefficient n was found to be less than 2, indicating a decrease in microhardness with increasing load. The increase in concentration of Li_2O , and ZnCl_2 or CdCl_2 in the glass composition was found to increase the rigidity of the glass structure and thereby to increase the microhardness. These results are in agreement with the results reported in the literature for other types of glasses.

4. Conclusions

Measurements of microhardness number H_v , were made on glass samples of composition $(1-x-y)(\text{B}_2\text{O}_3)-x(\text{Li}_2\text{O})-y(\text{MCl}_2)$, ($\text{M} = \text{Cd}, \text{Zn}$) for varying concentrations of MCl_2 and Li_2O . It was found that the microhardness of both the glass systems decreased with increase of load up

to 50 g and above a load of 100 g the hardness reached an almost constant value. The workhardening coefficient n was found to be less than 2, indicating a decrease in microhardness with increasing load. The increase in concentration of Li_2O , and ZnCl_2 or CdCl_2 in the glass composition was found to increase the rigidity of the glass structure and thereby to increase the microhardness.

References

- Bansal N P and Doremus R H 1986 *Handbook of glass properties* (New York: Academic Press) Ch. 4
- Ernsberger F M 1968 *J. Am. Ceram. Soc.* **51** 545
- Farkhonda Hassan, Osman El Mofty and Hamdy Kandil 1979 *Ceram. Bull.* **58** 1118
- Greenblatt S and Bray P J 1967 *Phys. Chem. Glasses* **8** 213
- Grodzinski P 1953 *Rev. Gen. Mecan.* **37** 147
- Hillig W B 1963 *Advances in glass technology* (New York: Plenum Press) p. 51
- Izumitani T and Suzuki I 1973 *Glass Tech.* **14** 33
- Kamitsos E I, Patsis A P, Karakassides M A and Chrysikos G D 1990 *J. Non-Cryst. Solids* **126** 52
- Konijnend W L 1976 *Phys. Chem. Glasses* **17** 205
- Mackenzie J D 1963 *J. Am. Ceram. Soc.* **46** 461
- Marsh D M 1961 *Proc. R. Soc.* **A279** 420
- Marsh D M 1964 *Proc. R. Soc.* **A282** 33
- Mott B W 1956 *Micro-indentation hardness testing* (London: Butterworths Scientific Publication)
- Neely J E and Mackenzie J O 1968 *J. Mater. Sci.* **3** 603
- Neill H O 1967 *Hardness and hardness measurements* (London: Chapman and Hall Ltd.) 2 ed.
- Onitsch E M 1950 *Mikroskopie* **95** 12
- Sagayaraj P, Sivanesan S, Baskar K and Gobinathan R 1990 *Cryst. Res. Tech.* **25** 1353
- Shrikhande V K, Mirza T, Sawant B B, Sinha A K and Kothiyal G P 1998 *Bull. Mater. Sci.* **21** 493
- Sreeram A N, Varshneya A K and Swiler D R 1991 *J. Non-Cryst. Solids* **130** 225
- Taylor E W 1950 *J. Soc. Glass Tech.* **34** 69T
- Varshneya A K 1994 *Fundamentals of inorganic glasses* (New York: Academic Press) Ch. 8 p. 177