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# The hardness of $PbO–ZnO–B_2O_3$ glasses

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Glasses were prepared within the ternary $PbO–ZnO–B_2O_3$ system and their microhardnesses were measured. Maxima in the hardnesses were found at about the 60 mol % $B_2O_3$ composition and were related to the glass structure. Trends of the hardnesses were explained in terms of the coordination of the boron and the effects of the PbO and ZnO on the structure as well as the void fraction within the glass. The hardnesses and the Young's elastic moduli were observed to be related and are also discussed.

## 1. Introduction

Glasses with low-temperature softening ranges are of interest for utilization in various electronic applications as solder glasses. An important oxide glass system for these applications is the ternary $PbO–ZnO–B_2O_3$ system [1], which has been extensively studied in terms of many of its properties, including its thermal expansion, viscosity and chemical durability. However, with the exception of elastic moduli and fracture toughnesses [2], most of the mechanical properties have not been systematically investigated, even though they are critical to many industrial applications. In this paper, a systematic study of the Vickers microhardness of several series of glasses in the $PbO–ZnO–B_2O_3$ system is reported and the trends are discussed in terms of the structural changes of the glasses and their void fraction.

## 2. Experimental procedures

Individual glasses within the glass forming region of the ternary $PbO–ZnO–B_2O_3$ systems were prepared at the PbO : ZnO molar ratios of 1 : 0, 3 : 1, 1 : 1, 1 : 3 and 0 : 1 for $B_2O_3$ contents of 30, 40, 50, 60 and 70 molar per cent. A total of 18 different homogeneous glasses were obtained, while several of the 50 and 60 mol % $B_2O_3$ compositions yielded immiscible melts. Chemical reagent grade red lead oxide (tetra), zinc oxide and boric anhydride were batched then melted in platinum crucibles in air for 1 and 1.5 h between 850 and 1200° C depending on the composition. During melting the glasses were stirred to aid in their homogenization. Plates were cast in 0.5 cm x 2.5 cm x 7 cm preheated stainless steel moulds and then immediately annealed. The end member compositions were analysed and are reported elsewhere along with additional sample preparation details [3].

In addition to measuring the microhardnesses, the densities were determined by the Archimedes method using kerosene at room temperature. Microhardnesses were determined on specimens which were successively polished with finer diamond pastes to a 1 μm final polish and then stored in a vacuum dessicator until immediately prior to measurement. The microhardnesses were determined using a Vickers diamond indentor by automatically applying a 100 g load over a 15 sec interval. The results are reported as the average and the 95% confidence interval for five distinct symmetrical indents for each composition.

## 3. Results and discussion

The Vickers microhardnesses of the glasses are listed in Table I. The softest glass was the 70 mol % PbO, 30 mol % $B_2O_3$ composition, only 287 kg $mm^{-2}$ while the hardest glass was the 20 mol % PbO, 20 mol % ZnO, 60 mol % $B_2O_3$ composition. It's hardness was 797 kg $mm^{-2}$, nearly three times that of the softest glass. It is evident from Table I that substituting ZnO for PbO increases the hardness of these glasses and that there appears to be a maximum in the hardness at near the 60 mol %

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TABLE I Room temperature Vickers hardnesses for the $PbO-ZnO-B_2O_3$ glasses

| PbO/ZnO (molar ratio) | $B_2O_3$ content | | | | |
|---|---|---|---|---|---|
| | 30 mol% | 40 mol% | 50 mol% | 60 mol% | 70 mol% |
| 1 : 0 | 287 + 8 | 380 + 5 | 433 + 19 | 554 + 32 | 525 + 14 |
| 3 : 1 | 345 + 11 | 454 + 12 | 554 + 22 | 612 + 29 | 599 + 24 |
| 1 : 1 | 380 + 7 | 498 + 21 | 685 + 28 | 792 + 30 | 673 + 24 |
| 1 : 3 | | 612 + 28 | 772 + 46 | | |
| 0 : 1 | | 681 + 48 | | | |

$B_2O_3$ composition for each PbO/ZnO molar ratio.

Fig. 1 illustrates these trends for the 18 homogeneous glasses and also depicts the results of Osaka *et al.* [4] for binary $PbO-B_2O_3$ glasses. The observed trends of this study are in good agreement with those of Osaka *et al.*; however, the individual microhardness values of the the two studies diverge at the higher $B_2O_3$ contents. This minor difference is probably the consequence of the numerous features of the microhardness test itself which lead to poor reproducibility as discussed by Ernsberger [5]. The important features of the two studies are their agreement of increasing hardness trends with $B_2O_3$ content and the existence of a microhardness maximum at about the 60 mol% $B_2O_3$ composition. Osaka *et al.* [4] attribute this hardness maximum to a maximum in the Pb–O bond strength, citing the study of Shartsis and Newman [6] which reports a heat of solution maximum in the same region.

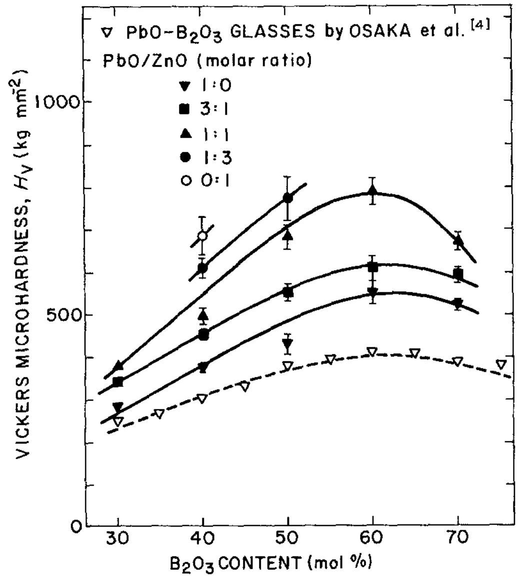

*Figure 1* Room temperature Vickers microhardness of the $PbO-ZnO-B_2O_3$ glasses.

Although no universally accepted process or mechanism for the hardness response of a glass has yet evolved, hardness has been related to a yielding of the glass structure [7, 8], a critical stress for densification [9, 10] and to plastic flow concepts [11, 12]. Since each of these processes may be envisioned as structurally dependent ones, it may be equally appropriate to simply relate the hardness trends to structural changes rather than to contrasting the aforementioned processes. The structure of various borate glasses has attracted the attention of a number of analysts and may be applied to explain some of the hardness trends in these glasses.

In the higher borate content glasses the structural changes induced by the addition of PbO and/or ZnO appear to be particularly significant and can be applied in conjunction with the structure's void fraction to explain the hardness trends. As indicated by Bray and co-workers [13, 14] the addition of PbO to $B_2O_3$ changes the boron coordination from 3 to 4 and the overall structure assumes more of a three-dimensional framework structure in contrast to a planar interlinking network of $BO_3^{3-}$ groups. As indicated by Makashima and Mackenzie [15], this increases the Young's elastic modulus of the structure. Furukawa and White [16] suggest that ZnO substitution for PbO simply tightens the glass structures without additional significant structural changes. According to Bray and co-workers [13, 14], the PbO (ZnO) initially is a structural modifier linking the $BO_3^{3-}$ and $BO_4^{5-}$ groups through two oxygens; however, at increasing PbO contents, the PbO participates in the network in the form of $PbO_4^{6-}$ pyramids. The introduction of PbO or ZnO also increases the void fraction of the open space with the glass structures. Since the improved three-dimensional framework character of the structure can be visualized to improve its resistance to shear flow and also to any densification in the vicinity of a hardness indentation, both can be visualized to

TABLE II Densities, molar volumes and calculated void fractions of the PbO–ZnO–$B_2O_3$ glasses

| Glass* | Density $\rho$ (g cm$^{-3}$) | Molar volume $V$ (cm$^3$ mol$^{-1}$) | Void fraction $\phi$ (%) |
|---|---|---|---|
| (30/1 : 0) | 6.858 | 25.83 | 44.9 |
| (30/3 : 1) | 6.322 | 24.09 | 43.7 |
| (30/1 : 1) | 5.727 | 22.26 | 41.2 |
| (40/1 : 0) | 6.192 | 26.12 | 42.2 |
| (40/3 : 1) | 5.800 | 24.22 | 39.7 |
| (40/1 : 1) | 5.167 | 23.07 | 38.9 |
| (40/1 : 3) | 4.490 | 21.81 | 37.7 |
| (40/0 : 1) | 3.687 | 20.79 | 37.0 |
| (50/1 : 0) | 5.730 | 25.55 | 37.2 |
| (50/3 : 1) | 5.293 | 24.31 | 35.7 |
| (50/1 : 1) | 4.756 | 23.33 | 34.8 |
| (50/1 : 3) | 4.113 | 22.67 | 34.7 |
| (60/1 : 0) | 5.063 | 25.88 | 34.3 |
| (60/3 : 1) | 4.602 | 25.39 | 34.3 |
| (60/1 : 1) | 4.096 | 25.07 | 34.8 |
| (70/1 : 0) | 3.267 | 27.11 | 33.8 |
| (70/3 : 1) | 4.037 | 26.02 | 32.0 |
| (70/1 : 1) | 3.671 | 25.72 | 32.1 |

*(30/1 : 0) refers to 30 mol% $B_2O_3$ and a PbO : ZnO molar ratio of 1 : 0.

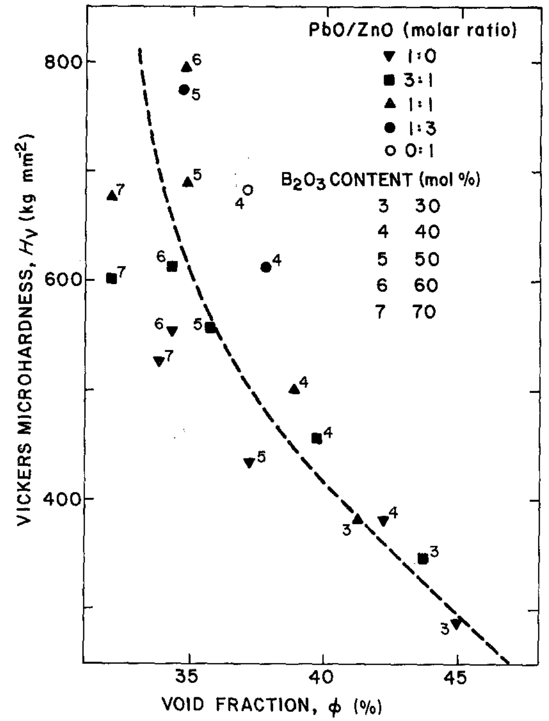

*Figure 2* The effect of void fraction on the Vickers microhardness of PbO–ZnO–$B_2O_3$ glasses.

increase the microhardnesses. In contrast, a more open structure containing a greater void fraction should be more susceptible to densification and thus exhibit a lower hardness. The contrasting effects of these two competing processes can result in a hardness maximum, similar to that in evidence in Fig. 1.

It is of interest to more directly examine the effects of the void fraction within these glass structures on the hardness, for it appears to relate directly to the ability of the glass to densify beneath an indenter. The void fraction $\phi$ of a glass can be defined as:

$$\phi = 1 - \left(\frac{V_0}{V_m}\right) \qquad (1)$$

where $V_m$ is the molar volume and $V_0$ is the volume occupied by the constituent ions. $V_0$ may be calculated from:

$$V_0 = \frac{4\pi}{3}\sum_i r_i^3 n_i \qquad (2)$$

where $r_i$ is the radius of each ion and the $n_i$ is the number per mole of each ion in the glass structure [4]. Applying ionic radii from the tabulation of Lange [17] yields the results summarized in Table II. These calculations reflect the openness of the structure when the PbO or (ZnO) content is increased as previously discussed.

Fig. 2 illustrates the effects of void fraction on the microhardness. It is evident that the higher void content glasses are the softest, as might be expected; however, perhaps even more significant is the scatter about the obvious trend line. The highest void content, lowest $B_2O_3$ content glasses exhibit almost an exact linear trend of decreasing microhardness with increasing void fraction, suggesting that the void fraction completely dominates the hardness in this structural regime. However, in the lower void content glasses, the scatter about the trend line is substantial, indicative of additional factors affecting the hardness. It is thus appropriate to attribute a significant portion of the hardness decreases between 60 and 30 mol% $B_2O_3$ to an increased openness of the glass structure. It appears significant that the void fraction dominates the hardness only for the lowest $B_2O_3$ content glasses and suggests that densification of the glass beneath the indentation may be particularly important for those glasses.

It is likely that it is the formation of $BO_4^{5-}$ and $PbO_4^{6-}$ groups and their contribution to the three-dimensional network structure, plus the dense

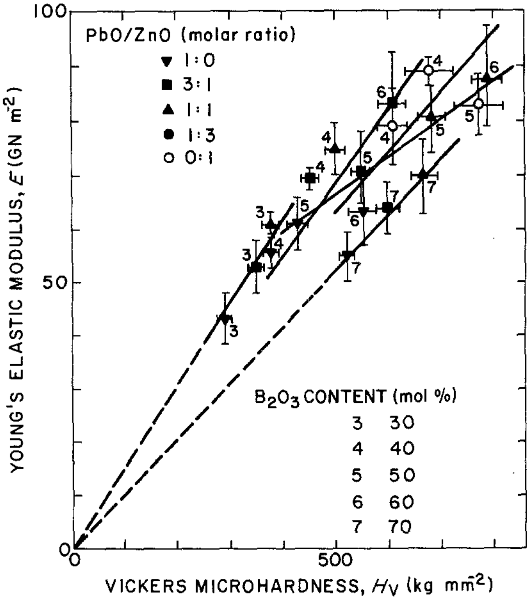

*Figure 3* The Vickers microhardness and Young's elastic modulus trends of the PbO–ZnO–$B_2O_3$ glasses.

packing of the structure which leads to the hardness maximum at about 60 mol % $B_2O_3$. The lower hardnesses at 70 mol % $B_2O_3$ for the glasses in this study and that of Osaka *et al.* [4] as well, also appear to be related to a structural effect. The Raman spectra of the 70 mol % $B_2O_3$ glasses [16] revealed a peak at 805 $cm^{-1}$ characteristic of a boroxyl group, although the lower $B_2O_3$ glasses did not. The result of Konijnendijk and Verweij [18] support this observation and suggest that the 70 mol % $B_2O_3$ glasses represent a structural transition from a higher $B_2O_3$ content boroxyl-group dominated structure to boroxyl-group-free glasses of lower $B_2O_3$ contents. The results in Fig. 1 suggest that the presence of the boroxyl group may be a contributing factor to the lower hardnesses of the 70 mol % $B_2O_3$ glasses.

Although it was previously noted that some controversy persists regarding the specific processes during hardness indentation of glasses, it is generally accepted that hardness and Young's elastic modulus are related [5, 19]. Fig. 3 illustrates the form of that correspondence for these glasses. It is evident that a general trend of increasing hardness with increasing Young's elastic modulus persists. It is also interesting that the different $B_2O_3$ contents, indicative of different glass structures lie on straight lines which extrapolate toward the origin. Even though the elastic modulus measurements are made at very small strains and the hardness indents produce extensive deformation, the effects of the glass structure are obviously very important in determining both properties.

The slope of the 30 mol % $B_2O_3$ glasses substantially exceeds the slope of the 70 mol % $B_2O_3$ glasses and together they form the bounds for the other compositions. At the 50 GPa Young's modulus level, the high $B_2O_3$ glass has a 50% higher hardness but only about a 25% more open structure. This clearly illustrates the importance of the void fraction as determined by the glass structure and presumably also the role of densification below the indentation in determining the hardness.

## 4. Summary and conclusions

A systematic study of hardness variations in the ternary PbO–ZnO–$B_2O_3$ glass system was completed at room temperature. It was observed that the microhardnesses varied by a factor of three within these glasses and exhibited a distinct maximum at about 60 mol % $B_2O_3$. The existence of this maximum in the hardness is related to the structure of these glasses, specifically the development of an extended $BO_4^{5-}$ plus $PbO_4^{6-}$ network and the openness or void fraction within the glass. The hardnesses also exhibit a direct relation to the Young's elastic moduli in a manner which reflects the existence of structural trends.

## References

1. A. E. DALE and J. E. STANWORTH, *J. Soc. Glass Technol.* 33 (1949) 167.
2. N. SHINKAI, R. C. BRADT and G. E. RINDONE, *J. Amer. Ceram. Soc.* 65 (1982) 123.
3. N. SHINKAI, PhD thesis in Ceramic Science, The Pennsylvania State University, University Park, PA 16802, USA (1979).
4. A. OSAKA, N. SOGA and M. KUNUGI, *J. Soc. Mater. Sci. Jpn.* 23 (1974) 128.
5. F. M. ERNSBERGER, in "Elasticity and Strength in Glasses", edited by D. R. Uhlmann and N. J. Kreidle (Academic Press, New York, 1980) p. 1.
6. L. SHARTSIS and E. S. NEWMAN, *J. Amer. Ceram. Soc.* 31 (1948) 213.
7. E. W. TAYLOR, *J. Soc. Glass Technol.* 34 (1950) 69.
8. L. AINSWORTH, *ibid.* 38 (1954) 479.
9. F. M. ERNSTBERGER, *J. Amer. Ceram. Soc.* **51** (1968) 545.
10. J. E. NEELY and J. D. MACKENZIE, *J. Mater. Sci.* 3 (1968) 609.
11. R. W. DOUGLAS, *J. Soc. Glass Technol.* 42 (1958) 145.
12. D. M. MARSH, *Proc. Roy. Soc. (London)* **282A** (1964) 33.

13. P. J. BRAY, M. LEVENTHAL and H. O. HOOPER, *Phys. Chem. Glasses* **4** (1963) 47.
14. M. LEVENTHAL and P. J. BRAY, *ibid.* **6** (1965) 113.
15. A. MAKISHIMA and J. D. MACKENZIE, *J. Non-Cryst. Solids* **12** (1973) 35.
16. F. FURUKAWA and W. B. WHITE, unpublished research.
17. N. A. LANGE, "Lange's Handbook of Chemistry", edited by J. A. Dean (McGraw-Hill, New York, 1973) pp. 3–118.
18. W. L. KONIJNENDIJK and H. VERWEIJ, *J. Amer. Ceram. Soc.* **59** (1976) 459.
19. J. D. MACKENZIE, Proceedings of the International Conference on the Mechanical Behaviour of Materials, Kyoto, August 1971, Vol. 4 (Society of Materials Science, Japan, 1972) p. 347.

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