

MICROHARDNESS OF ALKALI LEAD SILICATE GLASSES

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ABSTRACT

This work presents an experimental study done in an attempt to improve the microhardness of high-lead oxide shielding glasses. The partial substitution of inos of alkali metals (Li, Na, and K) for lead in a simple model glass (55.5 Pbo-45.5 Sio₂ in mo1%) was found to improve significantly its microhardness with a minimum sacrifice of its shielding power. The results here report indicate that small concentration (≈ 7 mo1% of Li⁺ inos replacing Pb²⁺ inos, increases the hardness of the investigated glass about 12% Such substitutions of alkali inos for lead, provided a small ternary region where the microhardness was improved without a significant loss in density and with even an initial gain. An empirical relation is proposed to correlate glass hardness with composition.

INTRODUCTION

In shielding windows a large cross section for absorbing high energy radiation involves considerable concentration of high-atomic-number elements. In oxide glasses the high valence of such elements generally introduces too much undesirable low-atomic-number oxygen. Lead represents an excellent compromise, since its electronic structure, characterized by two outer electrons, favors divalency despite its position in the fourth column in the periodic system, normally demanding valence four. Shand [1] indicated that lead has become a preferred constituent of high energy shielding glasses. Moreover, Weyl [2] reported that large amounts of lead can be incorporated in silicate systems in spite of the disruption of SiO₄ network generally giving glass stability. However, invariably such high lead glass systems are observed to have low values of microhardness. Several investigators have studied the indentation hardness produced in different glass systems in an attempt to understand the nature of these effects. There has been an argument whether microindentation hardness effect in glass occurs by densification or by plastic flow. Some researchers [3-5] studied the role of densification in deformation of glasses subjected to different transmitting media; such as, time temperature, pressure, and applied shear. They concluded that indentation is due primarily to densification of a volume of glass in

the vicinity of the indenter. On other hand, many other investigators have proven that indentation occurs by plastic deformation. Marsh [6], for example, has demonstrated that the stress around a hardness indenter during microhardness tests becomes higher than the yield stress, causing plastic deformation. More recently, the results obtained by Yoshimoto and Soga [7], upon studying the microhardness of lead silicate glasses, also hold the view that the indentation hardness of these glasses is an expression of microplasticity rather than densification. Their work also shows that the microhardness of these glasses decreases with increasing lead content due to the introduction of the weaker Pb-O bond into glass structure. Moreover, further work was done to study the structure and the elastic properties of these glasses. Imaoka et al, [8] proposed a structural model for lead silicate glasses in which chains of PbO₃ pyramids are connected with SiO₄ tetrahedra, and an increase in SiO₂ content leads to polymerization of silicate anions to longer chains, hence a stronger structure is attained. Mydlar et al, [9] showed that, at high lead content, nonlinking oxygen SiO₄ tetrahedra with structural units involving Pb-OPb bonds may appear leading to a weaker structure of lead silicate glasses. Another model of heterogeneous structure was adopted by Vernaz et al, [10] to explain the decrease in

toughness upon increasing lead content in silicate glasses containing 25-60 mol% PbO. Furthermore, Petzold et al, [11] measured the microindentation hardness of two glass sample in the $\text{Me}_2\text{O-PbO-SiO}_2$ system and found that the sample containing Na₂O has a greater hardness number than that containing K₂O) of a corresponding composition. A good overview of glass strength, structure, and relaxation is reported by Kurkjian [12]. In all events, swinging back and forth between structure and property has been always the acceptable rationale in controlling the different behaviour of engineering materials. As yet, and due to the complex nature of glass structure, no theory can satisfactorily explain the experimental results.

The present study attempts to provide a background for the improvement of the microhardness of lead-containing glasses, with minimum sacrifice of their shielding power, by the partial substitution of monovalent metals for lead. A simple model glass, 55.5 PbO-44.5 SiO₂, was chosen as base. It is also aimed to propose a mathematical relation that correlates the microhardness with composition of the present glass systems.

EXPERIMENTAL

Preparation of Glass

Some lead silicate glasses, in three different systems, were prepared. The systems investigated were alkali lead silicates of composition $x \text{ Me}_2\text{O}-(55.5-x) \text{ PbO}-44.5 \text{ SiO}_2$, where, x ranges from 0 to 7 mol% and Me_2O represents alkali or monovalent metal oxides; Li₂O, Na₂O, and K₂O. All samples were prepared from batches of 100 g. Silicon oxide was introduced in the form of fused silica, and lead oxide was introduced in the form of yellow lead oxide (litharge). Lithium oxide, Na₂O, and K₂O were introduced in the form of their respective carbonates. The chemicals used were all of analar grade and in powder form. After being thoroughly mixed, the batch constituents were put in a covered platinum-2% Rhodium crucible and then melted in an electrically heated furnace equipped with an automatic temperature control. The melting temperature of all glasses was $1250 \pm 10^\circ\text{C}$. To ensure good mixing, the batch was added in four steps (of 15 min interval) during the melting process and stirred till the melt solidified. The melt was left for three and half hour, then swirled once more and put back in the furnace for 30 min before casting. The molten glass was poured into a slightly heated steel mold of a rectangular shape base. The

glass samples obtained, having the dimensions 4x1x1 cm, were immediately transferred to the annealing furnace at a temperature 20°C below the glass transition temperature (Which was determined by differential thermal analysis). After one hour, the furnace temperature was decreased at a constant rate to room temperature in 24 hrs.

Measurement of Density

The density of the glass samples was measured at room temperature by hydrostatic weighing in para-xylene using a single germanium crystal as a reference. The reproducibility of the measured density was attained to a high degree of precision and values are considered accurate to within $\pm 0.003 \text{ g/cm}^3$.

Measurement of Microhardness

The microhardness of the glass samples was measured using the Vickers pyramid method reported by Zijlstra [13] and in accordance with the ASTM specifications (ASTM E 92) [14]. The glass samples were prepared for microhardness measurement by being lapped on both sides with aluminum oxide powder of 3 μ grain size and then finely polished using a 1 μm -polyurethane polisher. A semiautomatic miniload hardness tester was used. A load of 50 g for 10 s was found appropriate to obtain a crack-free Vickers indentation. In order to significantly improve the accuracy of measurements, 20 different indentations were made on each sample. The Vickers hardness number (H_v) obtained are considered accurate to within $\pm 1\%$.

RESULTS AND DISCUSSION

Density of Alkali Lead Silicate Glasses

Figure (1) shows the variation in glass density, of the presently studied alkali-lead-silicate glass systems, upon the gradual addition of Me_2O at the expense of PbO.

As expected from the atomic numbers, the density generally decreases as PbO is replaced by K₂O, Na₂O, or Li₂O. However, replacement by < 2% Li₂O leads to an increase in density. Moreover, the decrease in density by the substitution of alkali (K₂O > Na₂O > Li₂O) is in the opposite order as that of their atomic numbers. It is of great interest that consequently up to 2.6% Li₂O can be substituted for PbO without any loss in density; actually, an initial gain observed. The order of the effect of alkali is

in agreement with the influence of size of field strength (z/r^2), where z is the valence and r is the ionic radius, shown in Figure (2).

Li_2O (to a lesser degree Na_2O) permits an increase of microhardness without any significant loss in density. The order of the effect of alkali on glass hardness, shown in Figure (4), is also in agreement with the influence of field strength of the incorporated modifiers.

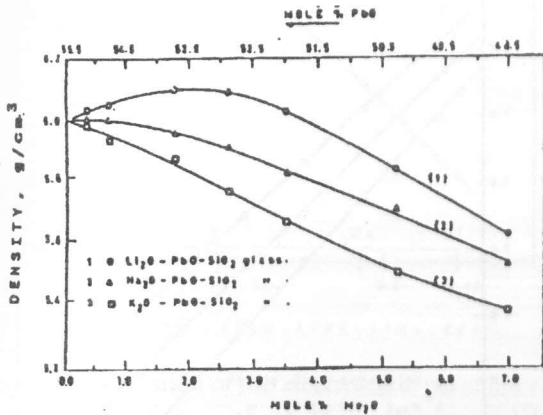


Figure 1. Change in glass density on addition of Me_2O at the expense of PbO in $x \text{Me}_2\text{O}-(55.5-x) \text{PbO}-44.5 \text{SiO}_2$ glasses.

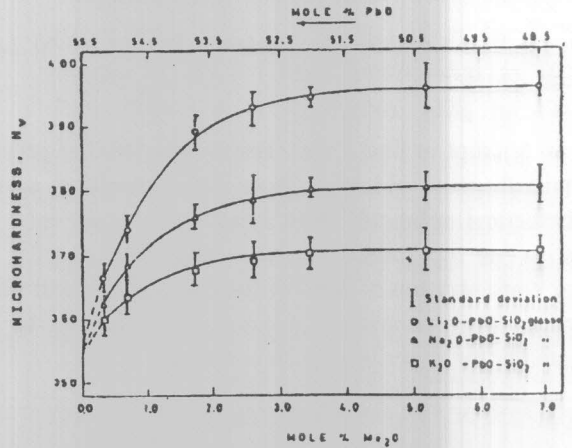


Figure 3. Effect of amount of Me_2O present on Microhardness in Alkali lead silicate glasses.

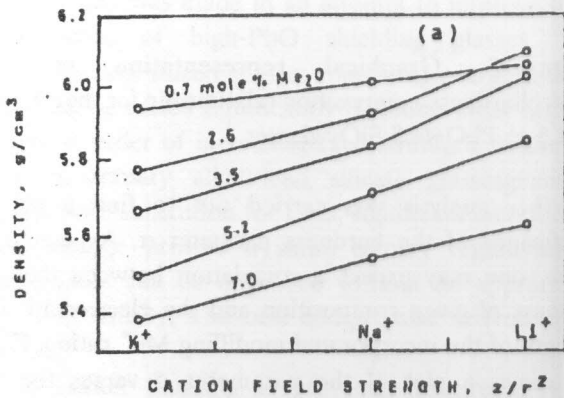


Figure 2. Correlation of Density with cation field strength of added monovalent metal ions in $x \text{Me}_2\text{O} (55.5-x) \text{PbO}-44.5 \text{SiO}_2$ Glasses.

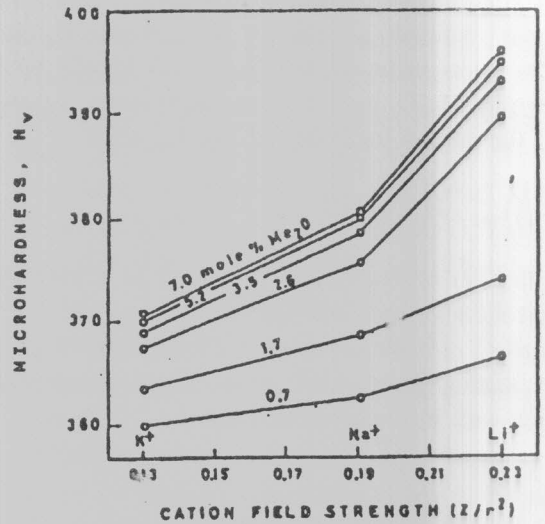


Figure 4. Correlation of microhardness with cation field strength of added monovalent metal ions in $x \text{Me}_2\text{O} (55.5-x) \text{PbO}-44.5 \text{SiO}_2$ glasses.

Microhardness of Alkali-lead-silicate Glasses

The effect of substituting k_2O , Na_2O . and Li_2O for PbO on microhardness is shown in Figure (3). In all cases, a substantial increase in microhardness is observed, in the order $\text{Li}_2\text{O} > \text{Na}_2\text{O} > \text{k}_2\text{O}$. Above ~ 3.5 the increase appears to saturate. The effect is attributed to the consolidation of the network when smaller ions substitute for PbO^{2+} . It is fortunate that in the alkali lead silicate ternary system a small region of initial substitution of

This behavior may well be interpreted by the screening approach to hardness, adopted by weyl and Marboe [15] and elaborated by Ray [16]. These authors suggested that glass under stress undergoes a disproportion of the inter-atomic forces, between the incorporated cations and the

anionic network, into weaker and stronger bonds and the magnitude of which is higher for ions of high polarizability (e.g. Pb^{2+}). Therefore, replacing Pb^{2+} ions by Me^+ cations would result in an increase in glass hardness, and the rate of increase in hardness is greater in glasses containing modifiers of smaller size.

Microhardness-Composition Relationship in Alkali Lead Silicate Glasses

In an attempt to find a correlation function that predicts the microhardness of a glass from its composition, several mathematical relations were tried to best fit into the variation of the measured glass microhardness with the molar concentration of Me_2 in the three alkali lead silicate systems. The following relation was found to be reasonable for describing such behavior.

$$H_v = H_{max} \cdot \beta \cdot e^{-\alpha x} \tag{1}$$

where, H_{max} is the maximum hardness attained when the rate of change in H_v is asymptotically zero with respect to the concentration x mol% of Me_2O , β is a hardness parameter defined as $(H_{max} - H_0)$ where H_0 is the microhardness value of base glass 55.5 PbO-44.5 SiO₂; i.e., zero% Me_2O , and α is an electrostatic parameter. Taking the natural logarithm of Eq.(1), yields

$$\ln (H_{max} - H_v) = \ln \beta - \alpha x \tag{2}$$

Equation (2) is graphically presented in Figure (5) as straight lines for the three investigated systems.

The slope of each line determines the value of q for the corresponding glass system. The obtained values of q , together with B , are given in Table 1.

Table 1. The Hardness Parameters α and B for Alkali Lead Silicate Glass Systems.

Me_2O	Li_2O	Na_2O	K_2O
α	0.938	1.022	1.138
β	41.5	25.5	15.5

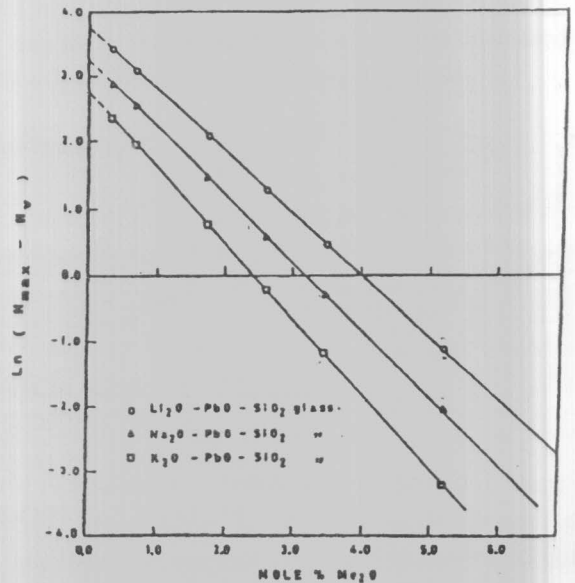


Figure 5. Graphical representation of the microhardness-composition relationship for the $x Me_2O$ -(55.5-x) PbO-44.5 SiO₂ glasses.

Further analysis was carried out to find a physical significance of the hardness parameter α . As mentioned above, one may expect a correlation between the glass hardness of given composition and the electrostatic field strength of the incorporated modifying Me^+ cation. Figure (6). shows a plot of the parameter α versus the field strength of the three cations Li^+ , Na^+ , and K^+ . This relation is found to be linear, with a negative slope of approximately 2, and may be represented by the following equation.

$$\alpha = - 2 (z/r^2) + C \tag{3}$$

where, C is a constant. Therefore, the hardness parameter α is thought to be electrostatic in nature. Combining Eqs. (2) and (3), the change in glass microhardness can then be described by an exponential function of the electrostatic parameter α and the concentration x of the modifying oxide (Me_2O) for a given glass system.

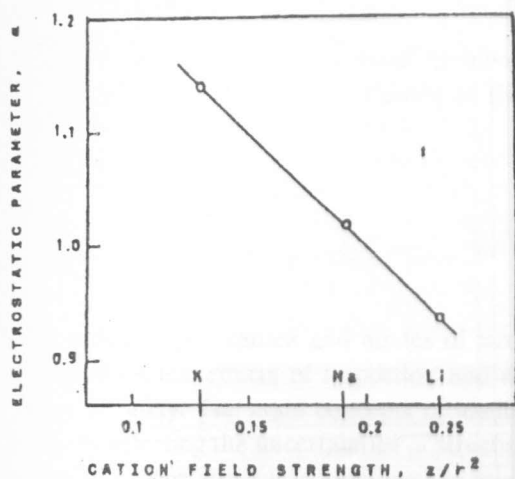


Figure 6. Correlation of the electrostatic parameter (a) with cation field strength of Me^+ incorporated in $x Me_2O-(55.5-x) PbO-44.5 SiO_2$ glasses.

CONCLUSION

In a model glass $55.5 PbO - 44.5 SiO_2$, substitution of Me_2O for PbO was made in an attempt to improve the microhardness of high- PbO shielding glasses. The microhardness of silicate glasses containing a large amount of PbO can be raised significantly by monovalent cations, generally in order of increasing field strength. While the density of ternary alkali-lead silicate glasses generally decreases with substitution for PbO , significant increases at low percentage provide a small ternary region where microhardness can be improved without an appreciable decrease in density. The best compromise involved up to ~3% Li_2O .

A correlation function is proposed to predict glass microhardness, within the three investigated systems, from the molar composition of each glass.

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