The effect of alkaline-earth ions on the mechanical properties of silicate glasses

Yordanos Bisrat, Russell J hand
Centre of Glass Research, Department of Engineering Materials, University of Sheffield, Sir Robert Hadfield Building, Mappin Street, Sheffield, S1 3JD, UK.

It is widely accepted that small surface flaws govern the strength of silicate glasses. Recently, Hand and Seddon suggested that defects with suitable properties to be strength controlling flaws could arise as a result of the interaction of atmospheric water and alkali channels in silicate glasses, which suggests that there should be systematic relationships between the strength and composition of silicate glasses. However there have been limited studies on the effects of composition on the mechanical strength of glasses. Kingston and Hand have shown that there is marked variation in strength and fracture toughness for mixed-alkali silicate glasses. This work has been further extended here to examine the effect of mixed-alkaline earths in silicate glasses. Therefore a range of soda-calica-magnesia, potassia-magnesia-baria and lithia-calcia-magnesia silicate glasses has been prepared and their mechanical properties, specifically fracture toughness, hardness and brittleness index, have been studied.

Introduction

There is little work reported in the literature on the effect of glass composition on the fracture toughness (K_{Ic}) and hardness (H) of glass systems. However, it has been shown that, at least for some glasses, K_{Ic} varies with composition in a complex way[i,ii]. In particular, Vernaz et.al[ii] have made systematic study of some binary and ternary silicate, borate and borosilicate glasses. They found that their experimental results were contradictory to the trends that might have been expected from existing structural models. They proposed a model[iii] based on micro-heterogeneous structure that produces nonannealable stresses in the material. They tested the model on some of the borosilicate glasses that they had previously studied and could explain some of the results observed. However, this model requires a refined knowledge of the glass structure for quantitative prediction.

More recently, Sehgal and Ito[iv] reported a scratch resistant glass produced by making compositional changes to a commercial soda-lime-silicate glass. Their work effectively suggests that both hardness and fracture toughness also vary with composition. Although no strength results are reported in their paper, because increased scratch resistance suggests that the development of surface defects should be reduced, it is possible that this scratch resistant glass also has improved mechanical strength compared to the conventional composition.

Most recently, Kingston and Hand[v] carried out systematic study on alkali-silicate glasses and obtained some evidence for the compositional effects on strength. Recent work in this laboratory also indicates that there are some compositional effects on strength, fracture toughness and brittleness for mixed alkali-alkaline earth silicate glasses.

This paper presents the mixed alkali-alkaline earth effect on the mechanical properties of silicate glasses. By doing so, it is hoped, it will be possible to shed some light on the elusive nature of Griffith flaws in silicate glasses.

Experimental procedure

Preparation of glasses

Three sets of glass compositions were studied. These compositions were chosen according to their ionic radius relationship. The potassia-magnesia-baria silicate glasses (series SKMB glasses where the ionic radius $r_{Ba} \sim r_K$) were melted in 300gm batches in Pt crucibles at 1450°C for 6hrs. For technical reasons the melts were not stirred but it was ascertained the melts were reasonably homogeneous. The glass melts were directly cast into steel moulds to make glass blocks for indentation. They were immediately annealed at 450°C for 1hr and then cooled to room temperature, using a cooling rate of 1^0C/min. For the lithia-calcia-magnesia silicate glasses (series SLCM glasses where the ionic radius $r_{Mg} \sim r_{Li}$) , 300gm of glass was melted at 1350^0C for 5hrs and after pouring into steel moulds, they were immediately annealed at 400°C for 1hr and then cooled to room temperature using a cooling rate of 1^0C/min. For the soda-calcia-magnesia silicate glasses (series SNCM glasses where the ionic radius $r_{Ca} \sim r_{Na}$), 300gm of glass was melted at 1450^0C for 5hrs. The glass melts were stirred with Pt stirrer for homogenisation and poured into steel moulds, and were immediately annealed at 540°C for 1hr and then cooled to room temperature using a cooling rate of 1^0C/min. After annealing, the glass blocks for all the glasses were cut, ground and polished to obtain a mirror finish samples for indentation. Fine ground sand and carbonates of the corresponding alkali and alkaline earth components were used as raw materials in each case.

Measurement of mechanical property parameters

Several indentations were performed using a standard Vickers indenter at each of the following loads, P: 24.5N, 49.0N 73.5N and 98.0N. For analysis, five indentations with well-developed cracks co-linear with the indentation diagonal and which emanated from the four corners of the indent were selected for each load. From these indentation patterns, the characteristic crack length (c) and indentation diagonal length (2a) were measured. The fracture toughness was then evaluated using [vi],

$$K_{Ic} = \frac{0.0824.P}{c^{3/2}} \qquad (1)$$

the hardness, H, using [vii]

$$H = \frac{P}{2a^2} \qquad (2)$$

and brittleness index, B, [iv]

$$B = \gamma P^{-1/4} \left[\frac{c}{a} \right]^{3/2} \qquad (3)$$

where $\gamma = 2.39\ N^{1/4}/\mu m^{1/2}$.

Results and discussion

Series SKMB glasses: both the hardness (H), and fracture toughness (K_{Ic}) show a peak at an intermediate composition (Figures 1a & 2a). This is rather odd behaviour from mechanics point of view. The brittleness index (B) on the other hand (Figure 3a) shows no significant variation for an intermediate composition reflecting the unusual concurrent increase in both K_{Ic} and H. It is believed, however, the increase in brittleness at the barium rich region may be because the larger size barium ions replacing the smaller magnesium ions results in a less open structure. In this case, deformation would not be easy and hence increased brittleness would result. This is consistent with the reports of Sehgal and Ito[iv] that when calcia was substituted with magnesia, the brittleness was lowered. It is however, not clear, if Sehgal and Ito have kept the other components constant as in our case.

Series SNCM and SLCM glasses: there seems to be a complex but similar variation of all the mechanical properties with composition for these series of glasses. Figures. 1b, 2b & 3b clearly show that there is some significant variation in properties which is less pronounced than with the SKMB glasses (Figures 1a, 2a & 3a), with changing alkaline earth composition. In this case when toughness increases the hardness and brittleness decreases as one would expect. On the other hand, because of the nature of CaO in enhancing depolymerization of the glass network, one may expect a noticeable lowering of fracture toughness at the CaO rich end of the series. However, the results as indicated in Figure 2b are contrary to this.

Comparing figures 1a and 1b, it can be seen that SLCM glasses have the highest hardness and that the hardness of SNCM glasses are similar although generally slightly larger than the hardness of the SKMB glasses. The SLCM and SNCM results suggest that as the alkali ion size increases ($r_{Li} < r_{Na} < r_K$) in otherwise analogous glasses the hardness decreases. The SKMB results are compatible with this observation although the change in alkaline earth species complicates the results and may explain the relatively similar hardness values for SNCM and SKMB glasses.

The toughness results are more complicated and it is difficult to determine a definite pattern. Yet, one can observe that the SLCM glasses have similar or lower toughness than the SNCM glasses which in turn have generally similar or lower toughness than the SKMB glasses. Thus, increasing alkali ion size may lead to higher toughness; however, more work is required to clarify this trend.

In light of the above results it is not surprising that the brittleness of SKMB glasses is less than that of the SNCM glasses which is in turn less than that of SLCM glasses. However, it is noticeable that the brittleness values of the SLCM and SNCM glasses are similar (in magnitude as well as following very similar pattern) which suggests that the alkaline earth ion size may be dominant in determining the absolute values of the brittleness.

Overall further work is required to confirm these trends however it does appear that there are significant variations of mechanical properties with composition and in particular with changing alkali and alkaline earth species. The relationships between mechanical properties and composition are clearly complex but the results here indicate that they may be potentially related to relative ion sizes.

Conclusions

Systematic studies were carried out to study the effect of mixed alkaline earth on mechanical properties of some glasses. Measurements performed for the fracture toughness, hardness and brittle index are reported for soda-calica-magnesia, lithia-calcia-magnesia and potassia-magnesia-baria silicate glasses. Significant variations with composition were observed. Tentatively, we propose that with the increase of the size of the alkali ion, the magnitude of fracture toughness increases (Figures 2a & 2b) and correspondingly both hardness (Figures 1a & 1b) and brittleness index decrease (Figures 3a & 3b). In addition, the magnitude of the brittleness index appears to be influenced more by the alkaline-earth species. Work is on going to confirm or clarify this hypothesis and related work to examine strength as a function of composition is also in progress.

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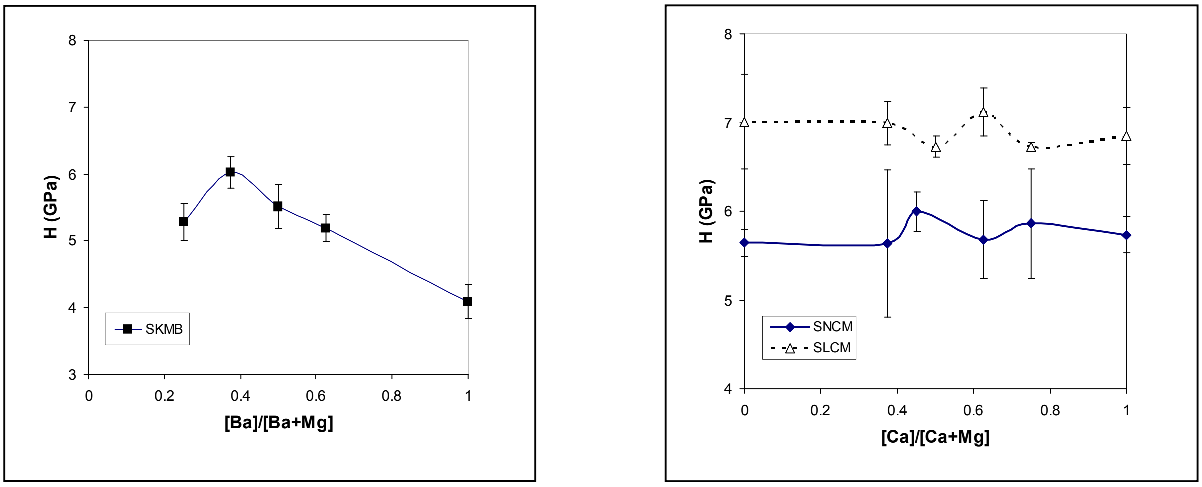

Figure 1: Hardness of a) SKBM glasses; and b) SNCM and SLCM glasses

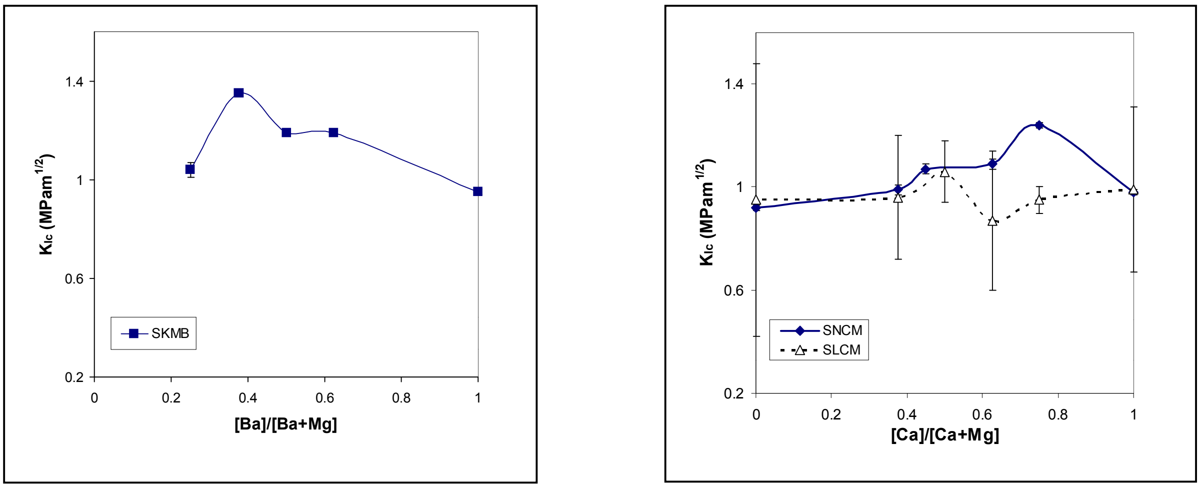

Figure 2: Fracture toughness of a) SKMB; and b) SNCM and SLCM glasses

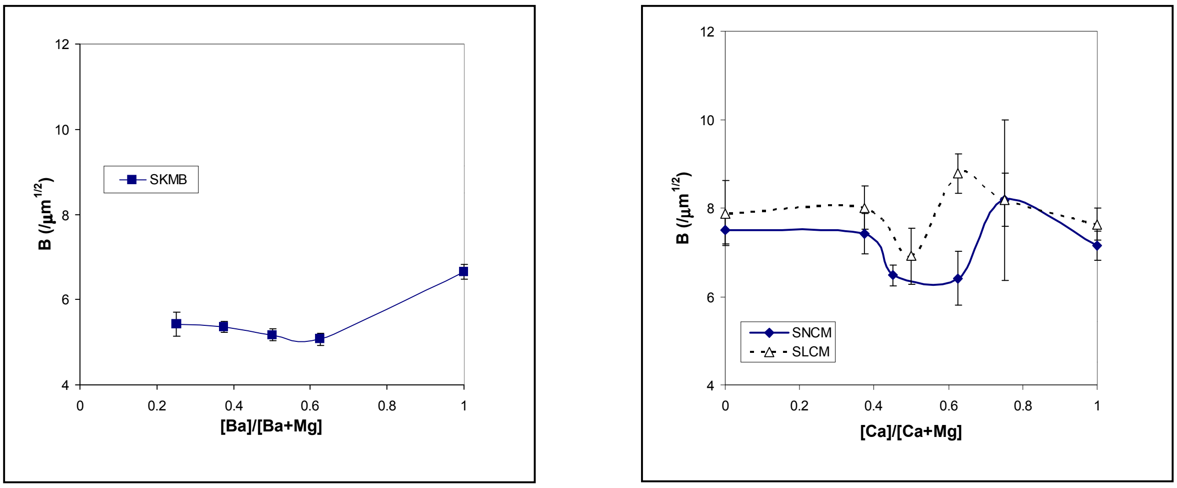

Figure 3: Brittleness index of a) SKMB; and b) SNCM and SLCM glasses

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