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Mechanical properties of soda–lime–silica glasses with varying alkaline earth contents

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ABSTRACT

The effects of varying the alkaline earth oxide content of three series of soda–lime–silica glasses with the general formulae $13.5Na_2O{\cdot}xMgO{\cdot}10CaO{\cdot}1.5Al_2O_3{\cdot}(75-x)SiO_2$ (mol.%) where $x = 0, 1, 2, 3, 4, 5, 6$, and 7; $13.5Na_2O{\cdot}3MgO{\cdot}(7+y)CaO{\cdot}1.5Al_2O_3{\cdot}(75-y)SiO_2$ (mol.%) where $y = 0, 1, 2, 3, 4, 5, 6$, and 7 and $13.5Na_2O{\cdot}zMgO{\cdot}(13-z)CaO{\cdot}1.5Al_2O_3{\cdot}72SiO_2$ (mol.%) where $z = 1, 3, 5, 7, 9$, and 11 have been examined. Raman spectroscopy and nuclear magnetic resonance (NMR) spectroscopy have been used to assess network connectivity. In the first two glass series network connectivity decreases with increasing alkaline earth addition whereas in the third series connectivity tends to be greater for the more magnesia rich glasses suggesting that magnesia does have a different effect to lime on network connectivity, but only when magnesia is the dominant alkaline earth species. Fracture toughness has been measured using bend testing, which avoids many of the questions raised by the widely used indentation technique. Moduli have been assessed using acoustic means. It was found that the mechanical properties tend to decrease with increasing network connectivity for all three glass series. For the $MgO–SiO_2$ series and $CaO–SiO_2$ glasses increasing the alkaline earth content at the expense of the silica content resulted in increased network depolymerization, whereas for the MgO–CaO series when MgO became the dominant alkaline earth species, network depolymerization was reduced. Thus whilst MgO and CaO both act as network modifiers when more CaO than MgO is present in soda–lime–silica glasses, a difference in behaviour is seen with magnesia rich soda–magnesia–silica glasses. In contradiction to previous data no significant advantage of replacing CaO by MgO is observed. In addition it appears that the glasses with the lowest fracture toughness values may be more resilient to contact damage than those with the higher fracture toughness values.

1. Introduction

There is a significant interest in reducing the weight and hence thickness of glass products in a number of applications [1] and this will require intrinsically stronger glass products [2]. Whilst very thin high strength glasses, such as Corning Gorilla® glass, are routinely produced for display applications, the processes used are expensive and not suited to bulk glass applications such as containers and glassware. Bulk glass production is based on a limited range of soda–lime–silica (SLS) compositions with 90% of all glass manufactured globally having this type of composition [3], albeit containing a range of other minor components. Even within a restricted compositional range some variation of mechanical properties with composition is to be expected and a number of authors have reported studies looking at such effects [1,2,4–7]. Most of the reported work is largely empirical, although Makashima and Mackenzie suggested an essentially linear model for calculating how the elastic moduli of a range of silicate and borate glasses vary with composition in the 1970s [8,9]. The more recent collection of Poisson's ratio data by Rouxel indicates that, at least some aspects, of this model are incorrect as the linear variation of Poisson's ratio with packing fraction predicted by the model was not observed [10].

Other work has given indications of non-linear variations in mechanical properties when one alkali is exchanged for another [4,5,7] with reduced ionic mobility in mixed alkali glasses apparently resulting in reduced plastic flow in indentation. In addition the literature indicates that alkaline earths also play an important role in controlling the mechanical properties. Thus the results of Deriano et al. [6] and Hand and Tadjiev [2] indicate that increased fracture toughness values may be obtained by increasing the MgO content, whilst reducing the CaO content at constant SiO_2 and Na_2O concentrations. The ionic radius and coordination number of Mg are smaller than those of Ca and thus substitution of MgO for CaO gives higher molar volumes which may explain the increase in fracture toughness [4]. Due to the small size of Mg there is also debate as to whether magnesium acts entirely as a network modifier [11] although the NMR results of Deriano et al. [6] indicate that, at least in the compositions they studied, MgO does

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behave as a network modifier in soda–lime–silica glasses. Alternatively the presence of smaller and mobile alkaline earth ions (Mg^{2+}) rather than larger less mobile alkaline earth ions (Ca^{2+}, Sr^{2+} or Ba^{2+}) might increase plastic flow, and consequently fracture toughness as observed for mixed alkali silicate glasses [7].

Another compositional factor that is expected to affect the mechanical properties of silicate glasses is changes in network connectivity. Thus increasing SiO_2 at the expense of alkali or alkaline earth oxides, thereby increasing the network connectivity is reported to enhance indentation fracture toughness [2]. Overall therefore the mechanical properties of silicate glasses do vary with composition and it would be beneficial to identify glasses with high fracture toughness values, as increased fracture toughness values can reasonably be expected to lead to increased strengths, although this does, of course, depend on the size of the strength controlling flaws that are present in the glass.

Hence in the current study, the effects of replacing SiO_2 with MgO or CaO, or replacing MgO by CaO with fixed SiO_2 content on the mechanical properties of glasses based on a simplified commercial soda–lime–silica glass composition are investigated. As well as measuring mechanical properties, Raman, infra-red and nuclear magnetic resonance (^{29}Si NMR) spectroscopies have been used to gain insight into the structural basis for the measured variations in the mechanical properties of the glasses.

2. Experimental

2.1. Sample preparation

Three series of glasses (MgO–SiO_2, CaO–SiO_2 & MgO–CaO series) have been produced. In the MgO–SiO_2 series the MgO:SiO_2 ratio was modified whilst in the CaO–SiO_2 series the CaO:SiO_2 ratio was modified. In both cases the concentration of all other constituents remained constant. In the MgO–CaO series the MgO:CaO has been modified whilst the concentration of all other constituents remained constant. The general formula of the MgO–SiO_2 series was $13.5Na_2O{\cdot}xMgO{\cdot}10CaO{\cdot}1.5Al_2O_3{\cdot}(75-x)SiO_2$ (mol.%) where $x = 0, 1, 2, 3, 4, 5, 6,$ and 7; that of the CaO–SiO_2 series was $13.5Na_2O{\cdot}3MgO{\cdot}(7+y)CaO{\cdot}1.5Al_2O_3{\cdot}(75-y)SiO_2$ (mol.%) where $y = 0, 1, 2, 3, 4, 5, 6,$ and 7 and that of the MgO–CaO series was $13.5Na_2O{\cdot}zMgO{\cdot}(13-z)CaO{\cdot}1.5Al_2O_3{\cdot}72SiO_2$ (mol.%) where $z = 1, 3, 5, 7, 9,$ and 11. Glass codes are of the form $M_pC_qS_r$ where p, q and r are the batched molar contents of MgO, CaO and SiO_2 respectively.

Batches to produce 300 g of glass were batched using SiO_2 (99.5%), Na_2CO_3 (99.1%), $CaCO_3$ (99.3%) (all from Glassworks Services), Na_2SO_4 (from Acros Organics), $4MgCO_3{\cdot}Mg(OH)_2{\cdot}5H_2O$ and $Al(OH)_3$ (both from Fisher Scientific). In most compositions, ~3 mol.% of the total Na_2O was supplied using Na_2SO_4 as a refining agent. The well mixed batch was transferred to a zirconia stabilized platinum crucible and heated to 1450 °C in an electric furnace for a total of 5 h. After allowing 1 h to achieve a batch free melt a Pt stirrer was inserted into the melt and the melt was stirred during the remaining 4 h of melting during which refining and homogenization occurred. Finally the molten glass was cast into a pre-heated stainless steel mould. After demoulding the still hot glass was transferred to an annealing furnace, where it was held at 560 °C for 1 h and then cooled to room temperature at a rate of 1 °C/min.

~20 × 20 × 3 mm samples were cut from the annealed glass bar on a Buehler ISOMET 5000. The samples were successively ground using MetPrep 120, 240, 400, 600, 800 and 1200 SiC grinding papers and finally successively polished using MetPrep 6 μm (oil based), 3 μm (oil based) and 1 μm (water based) diamond suspensions to achieve a mirror like finish. To remove residual stresses arising from the cutting, grinding and polishing the samples were re-annealed by heating to the annealing temperature at 1 °C/min, holding for 1 h and then cooling down to room temperature at a rate of 1 °C/min. A polariscope was used to check that the residual stresses had been removed by the re-annealing.

2.2. Chemical and physical measurements

The chemical compositions of the as-produced glasses were measured by XRF at Glass Technology Services, Sheffield. Density was measured using Archimedes' principle with distilled water as the immersion medium on a Mettler Toledo density balance. Differential thermal analysis was used to measure the glass transition temperatures of the produced glasses. A Perkin-Elmer Pyris 1 TGA was used. Fine powder samples were heated up to 1000 °C at a heating rate of 10 °C/min, cooled down to room temperature at the same rate and then re-heated up to 1000 °C again at 10 °C/min. The glass transition temperatures were obtained from the second heating curve using the in-built Perkin-Elmer software.

2.3. Structural analysis

Structural analysis was primarily conducted using Raman spectroscopy. Some samples were also studied using magic angle spinning nuclear magnetic resonance (MAS-NMR) to confirm the data obtained from the Raman analysis.

Raman spectra were obtained using a Renishaw InVia Raman Spectrometer. Before each test the instrument was calibrated using a Si wafer reference standard. Excitation of the polished and annealed glass surfaces was undertaken using a 514.5 nm laser at a laser power of 20 mW. The laser beam was magnified 50× and focused at a depth just beneath the polished surface. The exposure and acquisition times were both 10 s. The raw data were transferred to Labspec software and a baseline fitted by linearly connecting four points where the spectra goes to zero following the method of Colomban et al. [12]. This baseline was subtracted from the spectra which were then exported to Peakfitv4.12 software in order to calculate the area under the bands of interest.

^{29}Si NMR analysis of selected samples was undertaken using a Varian Unity Inova 300. 0.5–1.0 g of powdered sample was tested at the EPSRC National Solid State NMR service at the University of Durham, UK. The chemical shifts of the ^{29}Si NMR spectra of the samples are referenced to tetramethylsilane (TMS). Pulse angle, acquisition time and resonance frequency were set to 45°, 40.00 ms and 59.557 MHz respectively.

2.4. Mechanical property measurements

Hardness was assessed using Vickers indentation. The polished surfaces were indented with a load of 9.81 N for 20 s using a Mitutoyo Vickers indenter. The number of indentations made on each composition was ~10. The hardness was calculated using

$$H_V = \frac{1.854P}{d^2} \quad (1)$$

where d is the length of the indent diagonals.

Fracture toughness of the glasses was measured using bend testing with a controlled defect introduced via Knoop indentation in accordance with the BS EN ISO 18756: 2005 [13] standard. The samples were bars 3.5 × 4.0 × 46 mm on average, cut from the as-cast bulk glass blocks and the side to be placed in tension successively ground to a 600 grit finish. In order to prevent possible notch tip blunting, samples were annealed, prior to introducing the Knoop indentation at the centre of the 46 × 4.0 mm face using a 2 kg (19.62 N) load. The indentation process can introduce further residual stresses as well as lateral cracks, that might modify the stress intensity at the crack tip and consequently give erroneous fracture toughness values [14–17]. The standard therefore recommends grinding the indented surface of