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Mixed alkali effect on Vickers hardness and cracking

A. Mohajerani, J.W. Zwanziger *

Department of Chemistry and Institute for Research in Materials, Dalhousie University, Halifax, NS, Canada B3H 4J3

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ABSTRACT

Vickers indentation measurements were carried out on borate, silicate and aluminophosphate glasses, each series comprised of samples of different relative alkali ratios (Na/Na + Li). All the glass series exhibited non-linear variations of hardness with relative alkali ratio, which was attributed to the reduced plastic flow of mixed alkali glasses. The mixed alkali effect was also present in the length of radial cracks although less strongly than in hardness. Using a semi-empirical model, the variations of residual stresses and fracture toughness were estimated.

1. Introduction

Oxide glasses tend to exhibit non-additive variations of certain properties with the substitution of one alkali species by another at a total fixed concentration of alkalies. This phenomenon is known as the mixed alkali effect, or MAE, and is most noticeable in properties related to ion mobility, such as ionic conductivity and glass transition temperature [1–3]. Elastic properties of glass generally do not show significant mixed alkali effects, presumably due to the lack of ion mobility during elastic deformation [4,5].

Vickers indentation provides an attractive means of investigating MAE on the mechanical properties of glass, as it reflects a host of mechanical phenomena. The localized pressure at the indentation site is sufficient to plastically deform and densify glass, and to induce residual stresses that may form cracks of a variety of shapes. Of particular interest are radial cracks which initiate at the indent corners and grow in a radial direction outward the indent center (Fig. 1). The size of indents, *a*, and the length of radial cracks, *c*, are commonly measured to evaluate the hardness and fracture toughness of test materials, respectively.

The mixed alkali effect on the Vickers hardness of glasses has been reported previously [6,7]. Faivre et al. [6] measured Vickers indentation on an alkali aluminophosphate glass [0.50 P_2O_5, 0.04 Al_2O_3 0.46 xNa_2O–$(1–x)Li_2O$], $x = 0$, 0.5 and 1, at indentation loads of 100 g and 50 g. The size of the indents varied non-linearly with the relative alkali ratio, *x*, with the smallest indents on mixed alkali glasses. Using atomic force microscopy, they showed less pileup of material at the dent margins of mixed alkali glasses than those of single alkali glasses. Therefore, it was argued that reduced ion mobility in mixed alkali glasses hindered plastic deformation in mixed alkali glasses, thereby contributing to higher hardness values. Hand and Tadjiev also observed similar mixed alkali effect on the Vickers hardness of several series of silicate glasses of various Na_2O/K_2O ratios [7]. Mixed alkali effect on the indentation cracking of two series of silicate glasses of various Na_2O/K_2O ratios was investigated by Kingston and Hand [8]. Fracture toughness of glasses was calculated from the lengths of the radial cracks, which showed some or no mixed alkali effect depending on the content of CaO.

In the current study, the generality of MAE on glass hardness was investigated by examining three series of silicate, borate and aluminophosphate glasses. The mixed alkali effects on the residual stress and fracture toughness of these glasses were also estimated.

2. Methodology

2.1. Glass preparation

Three series of glasses were prepared, based on borate, silicate, and aluminophosphate. Each system was prepared with a fixed total alkali content but a variable ratio of sodium to lithium. The nominal compositions were $70B_2O_3$–$30M_2O$, $60SiO_2$–$40M_2O$, and $46P_2O_5$–$8Al_2O_3$–$46M_2O$. The alkali content, M_2O, ranged from 100% Li_2O to 100% Na_2O in steps of 25%. Glasses were synthesized from reagent grade B_2O_3, Al_2O_3, SiO_2, Na_2CO_3, Li_2CO_3 and $NH_4H_2PO_4$. Alumina was only added to the aluminophosphate glasses in order to reduce their hygroscopy.

Phosphate, borate and silicate glasses were melted at 1100°, 1200°, and 1550°, respectively. They were melted in air in a platinum crucible and then cast into a brass mold. Glasses were then annealed for two hours at the glass transition temperature, T_g. Because of the high amount of carbonate in the aluminophosphate glasses, the raw material was added to the crucible in several steps at 600° before

* Corresponding author.
E-mail address: jzwanzig@dal.ca (J.W. Zwanziger).

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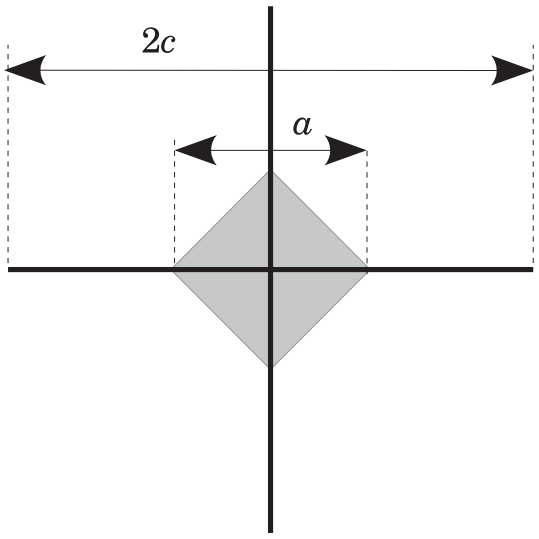

Fig. 1. Schematics of indents and radial cracks on the indented plane. Radial cracks grow from the indent margin and grow radially outward from the indent center.

melting. The specimens were cut into blocks and polished with sand papers in a sequence of finer grits to the grit size of 1200.

2.2. Physical measurements

The densities of the glasses were measured at room temperature using the Archimedes method with absolute alcohol as the immersion fluid. The accuracy of the measurements was approximately ± 0.02 g cm^{-3}.

The compositions of glasses were analyzed using Energy Dispersive X-Ray Spectroscopy, EDS, for the phosphate and silicate series, and density measurements for the borates and lithium silicate. For the silicate and phosphate series, EDS showed the compositions to be close to the nominal compositions (Table 1), while for the borate and lithium silicate glasses, the densities were within 1% of literature values (Table 2).

The glass transition temperatures of glasses were determined by differential scanning calorimetry on a TA Instruments Q200, at a heating rate of 10°min^{-1} in an N_2 environment. The precision of the measurements was approximately ± 2°.

Young moduli, E, shear moduli, G, and Poissons ratio of the glasses were calculated from the ultrasonic wave velocities. Bulk modulus, K, was subsequently calculated from the values of E and G. The ultrasonic

Table 1
Nominal glass compositions, and nominal and measured atomic ratios from Energy Dispersive X-ray Spectroscopy.

	Na/Si	
Batch	nom	expt
$60SiO_2$–$40Li_2O$	0	
$60SiO_2$–$30Li_2O$–$10Na_2O$	0.33	0.35
$60SiO_2$–$20Li_2O$–$20Na_2O$	0.68	0.69
$60SiO_2$–$10Li_2O$–$30Na_2O$	1.00	1.07
$60SiO_2$–$40Na_2O$	1.33	1.17

	Al/P		Na/P	
Batch	nom	expt	nom	expt
$46P_2O_5$–$8Al_2O_3$–$46Li_2O$	0.17	0.16		
$46P_2O_5$–$8Al_2O_3$–$34.5Li_2O$–$11.5Na_2O$	0.17	0.17	0.25	0.23
$46P_2O_5$–$8Al_2O_3$–$23Li_2O$–$23Na_2O$	0.17	0.16	0.50	0.50
$46P_2O_5$–$8Al_2O_3$–$11.5Li_2O$–$34.5Na_2O$	0.17	0.16	0.75	0.77
$46P_2O_5$–$8Al_2O_3$–$46Na_2O$	0.17	0.16	1.00	0.88

Table 2
Nominal glass compositions and experimental densities in units of g cm^{-3}. The densities are compared to literature values; for the glasses with 22.5, 15, and 7.5 mol-% Li_2O the comparison is to the values interpolated from the data of ref. [9]. Experimental uncertainty ± 0.01 g cm^{-3}.

Batch	Expt. density	Ref. density
$70B_2O_3$–$30Li_2O$	2.22	2.23 [9]
$70B_2O_3$–$22.5Li_2O$–$7.5Na_2O$	2.27	2.26 [9]
$70B_2O_3$–$15Li_2O$–Na_2O	2.28	2.29 [9]
$70B_2O_3$–$7.5Li_2O$–$22.5Na_2O$	2.31	2.31 [9]
$70B_2O_3$–$30Na_2O$	2.33	2.35 [9]
$60SiO_2$–$40Li_2O$	2.33	2.35 [10]

longitudinal and shear wave velocities at room temperature were obtained by the pulse-echo-overlap technique using a Panametrics-NDT system. The uncertainty of the measurement of the wave velocity was ± 17 ms^{-1} in the longitudinal mode and ± 12 ms^{-1} in the shear mode.

The hardness measurements were carried out on a micro-hardness Vickers tester and a macro-hardness Vickers tester depending on the amount of load. The measurements were taken twice, once immediately after polishing, and the other a week after. The variations of the test results in this time span were within the experimental error. Vickers hardness, H_V, was calculated as the ratio of the load, F, to the surface area of the indent, A, indented plane as

$$H_V = \frac{F}{A} = \frac{1.8544F}{a^2}. \quad (1)$$

The size of the indents was measured immediately after the indentation, using an optical microscope. The lengths of the cracks were measured 1°min after the indentation, when their lengths were significantly stabilized.

To investigate indentation creep of glasses, indentations were performed at different loading times (5 s, 10 s, 30 s). In all glasses, indent size remained unaffected by the loading time, indicating negligible indentation creep at room temperature. This observation suggests that indentation creep in oxide and non-oxide glasses is quite different, as Ge–Se glasses present noticeable indentation creep in the initial 30 s of indentation loading [11].

3. Results

All the three glass series exhibited nonlinear variation of Vickers hardness, H_V, with the alkali ratio, with maximum values appearing for relative alkali ratio of approximately 0.5 (Fig. 2). Measurements were repeated for different indentation loads, showing very similar mixed alkali effect, although the absolute values of hardness slightly increased with decreasing load.

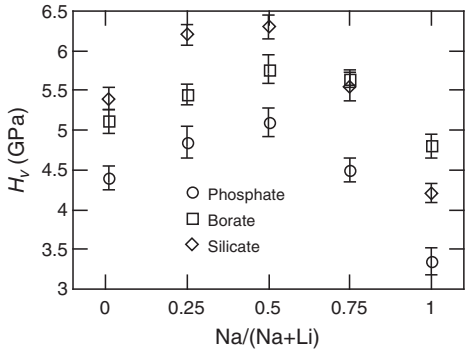

Fig. 2. Vickers hardness of glasses as a function of alkali ratio, at the indentation load of 0.2 kg. The symbols show the mean of five measurements at random locations, and the error bars show the corresponding standard deviations. The legend shows glass series.