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LETTER TO THE EDITOR

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Letter to the Editor

Densification and plastic deformation under microindentation in silicate glasses and the relation to hardness and crack resistance

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ABSTRACT

To quantify and study the densification and plastic deformation under Vicker's indentation we prepared a series of simple soda-lime-silicate glasses with different modifying ion contents and four glasses with constant silica content but potassium and/or barium substituted for sodium and/or calcium. The densification and plastic deformation in these glasses were determined using atomic force microscopy (AFM) by measuring each sample twice, i.e., once immediately following indentation, and once after annealing to relax the densified volume. The results show that the densified volume of the glasses decreases approximately linearly with the bulk modulus, and the plastic deformation volume with silica mole fraction. These results have important implications in the prediction of hardness and crack resistance (i.e. load for crack initiation) from composition.

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1. Introduction

With the advent of flat panel display glasses for TV, monitors, and touchscreen devices, surface mechanical properties, such as scratch and fracture resistance emerge as important material properties [1]. These properties are usually evaluated using the method of microindentation of glasses by relating hardness to scratch resistance, and relating the crack resistance (or load for crack initiation) to fracture resistance [2]. Despite the profusion of microindentation measurements the deformation processes occurring under indentation are not well understood, and this inhibits a deep understanding of the properties measured through microindentation. The three deformation processes are an elastic deflection of the surface fully recovered upon unloading, a volume-conservative plastic flow induced by the gigapascal-range shear stresses, and a non-volume conservative densification of the structure in a hemispherical region under the indent [3]. A physical understanding of these deformation processes is crucial for establishing accurate predictive models of indentation related properties. For example, the deformation mechanisms are used in a semi-empirical model to calculate indentation hardness from composition [4]. The model predicts hardness quite well using only qualitative data for the compositional variation of the deformation mechanisms. More recently, a promising approach for predicting the glass hardness from chemical compositions has been established, which is based on the temperature dependent constraint theory [5]. The hardness values of a soda-lime-borate glass series can be predicted by using this approach and are in good agreement with the measured ones. However, temperature dependent constraint theory does not take into account the different deformation processes occurring during indentation, and this is exactly what the authors give as the key reason for discrepancies between the calculated and measured hardness values when extending the method to borosilicate glass compositions [6]. A relation between the fracture of glass and the relative contributions of densification and plastic deformation has been suggested by Kato and his co-workers [7–9]. They found that crack initiation is governed by residual stress induced by plastic deformation. As the plastic deformation increases with applied load the residual stress will reach a critical value at some point, and cracks will initiate. Although the plastic deformation universally increases with applied load (and the relative amount of densification decreases), there are significant differences in the degree of plastic deformation exhibited by the investigated glass compositions; thus leading to cracking occurring at different loads.

Therefore, we believe that quantitative knowledge of the compositional dependence of the different deformation mechanisms will be useful for the prediction of indentation related properties, such as hardness and crack resistance. In the present work we determine the contribution by volume of plastic deformation and densification in a series of soda-lime-silicate model glasses, and also investigate the effect of substituting Na_2O for K_2O and/or CaO for BaO on both the hardness and the deformation volumes at constant silica content. The relative amount of densification is known to decrease with load, even so, the effect of composition is clearly discernible [9]. The deformation volumes will be determined at a single load in order to focus

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Table 1
Nominal compositions of the silica-sodium oxide–calcium oxide (SNC) series with changing silica content and modifier substituted compositions with constant silica content but changing modifying ions used in this work. The glass names are used throughout the text and figures.

Glass name	Oxide (mol%)					T_g[a] (K)
	SiO_2	Na_2O	CaO	K_2O	BaO	
80SNC	80.0	15.0	5.0	–	–	814
75SNC	75.0	25.0	–	–	–	763
71SNC	71.4	23.8	4.8	–	–	786
68SNC	68.2	22.7	9.1	–	–	806
65SNC	65.2	21.7	13.0	–	–	818
60SNC	60.0	20.0	20.0	–	–	831
75S15K10B	75.0	–	–	15.0	10.0	841
75S15N10B	75.0	15.0	–	–	10.0	727
75S15K10C	75.0	–	10.0	15.0	–	903
75S15N10C	75.0	15.0	10.0	–	–	841

[a] Measured by dilatometer. Error is estimated to be ±3 K [22].

on the effect of glass composition. We attempt to relate the hardness and the measured deformation volumes to the elastic moduli, as these represent resistances to different deformation modes in the elastic regime, and are thought to be related to the resistances to permanent deformation as well. We also measure the crack resistances of the compositions exhibiting the lowest plastic deformation volumes.

2. Experimental

The glasses were prepared from analytical reagent-grade raw materials: SiO_2, Na_2CO_3, $CaCO_3$, K_2CO_3 and $BaCO_3$ powders. The glass compositions are given in Table 1. The raw materials were mixed and melted at 1575 °C for 2 h in a platinum crucible. After this the melt was cast, crushed, and re-melted for 1 h, then quenched on a brass plate and immediately annealed at the glass transition temperature (T_g) for 2 h, and cooled at 1 K/min. T_g was determined with a heating rate of 10 K/min using a dilatometer (TMA/SS6000, Seiko Instruments Inc.), density by the Archimedes method in toluene, and elastic moduli by ultrasonic measurement of the velocity of sound (DPR300, JSR). Coplanar samples polished to a mirror finish were prepared and used for Vicker's microindentation (MVK-H2, Akashi). Twenty crack-free indentations were made at 245 mN (the highest load giving crack-free indents for all compositions) and 15 s dwell time, and then imaged by atomic force microscopy (AFM, SPA400, Seiko Instruments Inc.). The samples were annealed at $0.9T_g$ for 2 h to relax the densified volume [10] and imaged again by AFM. Densified and plastic deformation volumes were calculated as specified in [11]. Before initiating crack resistance measurements all samples were acclimatised for 24 h to the testing conditions (25 °C and 30% relative humidity). The crack resistance was determined as the load at which an average of two cracks initiated from the corners of the indent. Twenty Vicker's indentations (MXT50, Matsuzawa) were made at five to seven loads on each sample.

3. Results

The variations of Vicker's hardness, plastic deformation volume and densified volume with composition are shown in Fig. 1a and b. The Vicker's hardness varies widely across the investigated compositions, ranging from 3.7 GPa to 5.2 GPa with no apparent compositional trend. The densified volume generally increases with silica content, but with large scatter. The plastic deformation volume however is well described by the silica content. It is attempted to relate the Vicker's hardness and deformation volumes to the elastic constants of the glass compositions. It is found that the Vicker's hardness correlates well to the Young's modulus (Table 2), and the variation in densified volume is described well by the bulk moduli (Fig. 2a), yet the change in plastic deformation volume shows no compelling relation to an elastic constant, but is described best by the silica contents (Fig. 2b). The volume recovery ratio, defined as the ratio of recovered densified to the total deformation volume (equal to the volume of the indent [11]) is plotted against composition in Fig. 3a. The volume recovery ratio increases strongly and approximately linearly with silica content, ranging from about 20% at 60 mol% silica to about 100% at 80 mol% silica. The volume recovery ratio has previously been linked to the Poisson's ratio [11–13], and this relationship is plotted in Fig. 3b. Fig. 4 shows the data and procedure for determining the crack resistances of three compositions exhibiting low plastic deformation volumes. The crack resistances were determined to be 7.0 N ± 2 N for 80SNC, 1.1 N ± 0.2 N for 75S15K10C and 1.0 N ± 0.1 N for 75S15N10C.

4. Discussion

Of the four elastic constants listed in Table 2 it is Young's modulus that best correlates with the Vicker's hardness. Such an empirical relation is well known, but has significant scatter [14,15]. The correlation could be an indication that the elastic deformation largely determines the indentation hardness, which fits well with the finding from nanoindentation studies that the work of elastic deformation is commonly larger than that of permanent deformation [16]. A strong correlation between the densified volume and the bulk modulus was discovered (Fig. 3a). Since the bulk modulus is the elastic resistance to hydrostatic compression, and approximately two-thirds of the mean pressure beneath the indenter is hydrostatic [17], densification occurs when the elastic compression reaches a certain yield value by increasing pressure. Such a yield compression has been observed for a variety of glasses under high pressure

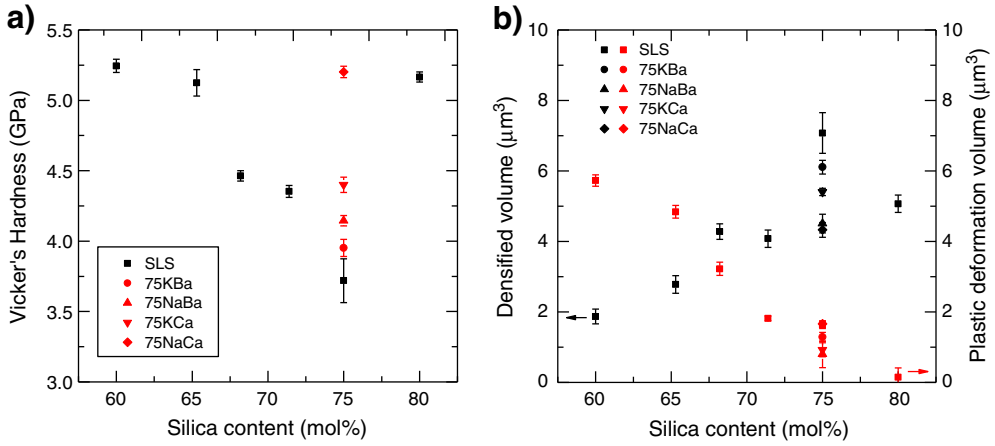

Fig. 1. a) The compositional variation of Vicker's hardness, and b) densified and plastic deformation volume. Arrows: The axis on which the densified volume and plastic deformation volume should be read.

Table 2
The physical and mechanical properties of the studied glasses: density (δ), Poisson's ratio (ν), Young's modulus (E), bulk modulus (K), shear modulus (G) and Vicker's hardness measured at 245 mN and a dwell time of 15 s (H_v).

Glass	δ (g/cm^3)	ν (–)	E (GPa)	K (GPa)	G (GPa)	H_V (GPa)
80SNC	2.412	0.21	67.6	39	27.9	5.2
75SNC	2.435	0.23	59.2	37	24.1	3.7
71SNC	2.480	0.24	65.2	41	26.4	4.4
68SNC	2.524	0.25	68.8	45	27.6	4.5
65SNC	2.572	0.25	72.3	48	29.0	5.1
60SNC	2.637	0.26	77.9	53	31.0	5.2
75S15K10B	2.445	0.25	52.0	34	20.8	4.0
75S15N10B	2.461	0.26	58.5	40	23.3	4.2
75S15K10C	2.468	0.23	62.7	39	25.4	4.4
75S15N10C	2.484	0.22	71.4	43	29.2	5.2
Max. error	±0.001	±0.01	±0.6	±1.4	±0.3	±0.1

hydrostatic compression [18]. Since a higher bulk modulus is probably related to higher yield value, glasses with higher bulk modulus have lower densification volumes at a given load.

As shown in Fig. 2b, the plastic deformation volume decreases linearly with the silica mole fraction. Given this relation, it is interesting to note that amorphous silica is generally believed not to deform plastically on indentation [19], and the volume recovery ratio has previously been determined to be 92%±4% at a load of 100 mN [11]. The effect of the modifying ion on the plastic deformation is rather small, with the plastic deformation volumes for the 75 mol% SiO_2 glasses ranging from 0.8 μm^3 to 1.7 μm^3, with a maximum standard deviation of 0.6 μm^3. The influence of the type of modifying oxides tested here (Na_2O, K_2O, CaO and BaO) is small relative to the influence of the silica content on the plastic deformation volume. The effect could be caused by silica constituting the major component in the compositions, and thus masking the influence of the type of modifying oxides. However, it has been proposed that the mechanism of plastic deformation in glasses is slipping between modifier rich planes in the structure due to their relatively low bonding energy [19]. Another interpretation of the observed phenomenon is that the type of modifier does not affect the plastic deformation volume much, because they per definition have the weakest bonds in a silicate glass, and the exact strength of these weak bonds is less important than their concentration. It is interesting to note that the plastic deformation tends to zero around 80 mol% silica, which corresponds quite well to the concentration where modifier rich channels start forming according to the modified random network model [20]. The volume recovery ratio is an important parameter in that it does not change as drastically with load as the deformation volumes. The volume recovery ratio is found to increase approximately linearly with the silica mole fraction, although the 75S15N10C composition deviates from the trend (Fig. 3a). This fits well with the plastic deformation volume decreasing with the silica content. The relation to silica mole fraction is more compelling than the one previously suggested to Poisson's ratio [11–13], as shown in Fig. 3b. Poisson's ratio is an elastic constant that can be interpreted as a measure of the relative susceptibility to shear deformation versus hydrostatic compression; a material with low Poisson's ratio is easily compressed, but difficult to

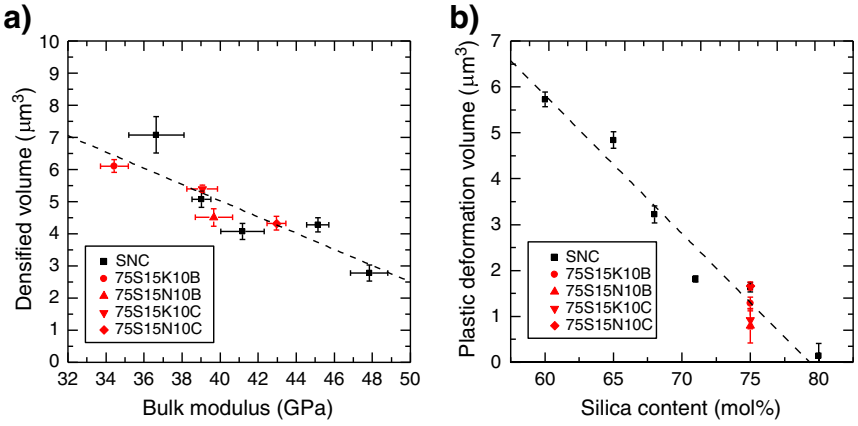

Fig. 2. a) The best fit to the densified volume under a 245 mN indent as measured by AFM was found to be the bulk modulus (K). b) For the plastic deformation volume the silica mole fraction gave the best fit. The dashed lines are the best linear fits to the data.

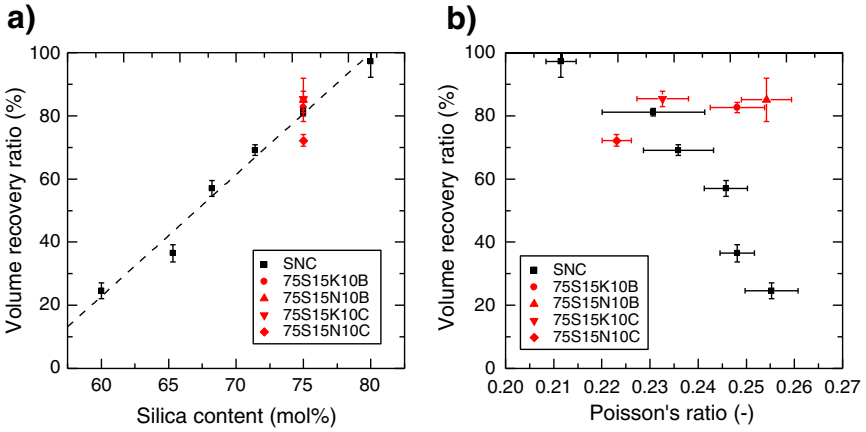

Fig. 3. a) The volume recovery ratio (ratio of densified volume to total deformation volume) as a function of the silica content. The dashed line is the best linear fit to data. b) The volume recovery ratio as a function of Poisson's ratio.

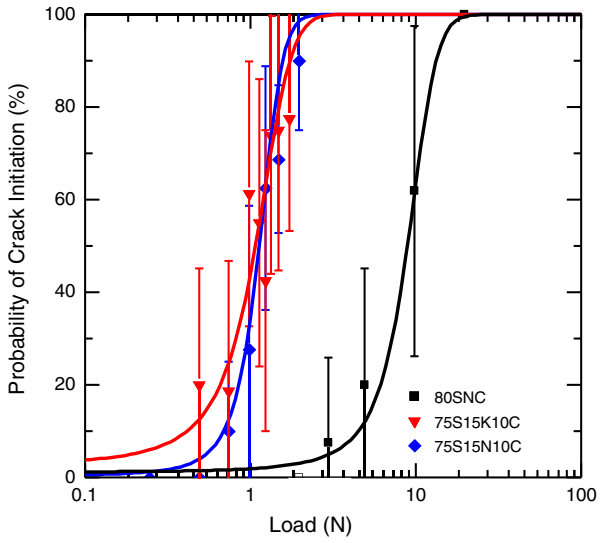

Fig. 4. The probability of crack initiation at different applied loads. The probability is determined as the average number of radial cracks per corner out of 20 indents at a given load. The crack resistance is the load where the probability of crack initiation is equal to 50% (i.e. on average two corners out of four will contain cracks). The crack resistances are determined from a sigmoidal fit to the data.

shear, while $\nu = 0.5$ describes a perfectly incompressible material [18]. That the relation between the volume recovery ratio and Poisson's ratio is not very convincing is in agreement with the plastic deformation volume apparently not being strongly correlated with the shear modulus. This is surprising, and may be caused by the inherent nanometer-scale heterogeneity of glass, namely the modifier channels previously mentioned [20].

The 80SNC composition is known to have low brittleness [2], which normally indicates high crack resistance, but the crack resistance has not previously been determined. We show that the 80SNC glass composition has approximately zero plastic deformation at 245 mN, and that the crack resistance is about seven times larger than that of the 75S15K10C and 75S15N10C compositions (see Fig. 4). The latter compositions have higher plastic deformation volumes at 245 mN. This suggests that the silica content of a glass has a large impact on both crack resistance and plastic deformation volume. Although the load dependence of the plastic deformation has not been taken into account, this supports the work reported in [7–9], where it is believed that the plastic deformation induces residual stress that causes cracking. Other highly crack-resistant glasses also have silica contents around 80 mol%, such as $80SiO_2 \cdot 10Al_2O_3 \cdot 10CaO$ with crack resistance of ~10 N in a nitrogen glove bag [1], and Asahi less-brittle glass of composition $79SiO_2 \cdot 2Al_2O_3 \cdot 13Na_2O \cdot 1K_2O \cdot 4MgO \cdot 1CaO$ that does not crack at loads up to around ~35 N in a nitrogen glove box [2]. Our results suggest that these high crack resistances are obtained largely because of the low plastic deformation volumes, or conversely large volume recovery ratios of high silica glass. However other factors are known to play a role, like the load dependence of the plastic deformation, but also the susceptibility to water in the atmosphere. For example, amorphous silica has a crack resistance around ~2.5 N in a nitrogen glove bag [1], yet can achieve crack-free indentations up to ~10 N under identical conditions by etching away the hydrated surface layer [21].

5. Conclusions

A quantitative correlation of densified volume, plastic deformation volume, and the volume recovery ratio to elastic constants and composition has been reported. As hardness must ultimately be governed by the resistances to the individual deformation processes occurring during indentation, this discovery could lead to an improved predictive hardness model. Our results are also relevant for describing the compositional dependence of the crack resistance. We show that the crack resistance of an 80 mol% SiO_2 composition is ~7 N, compared to around ~1 N of the 75 mol% SiO_2 compositions. We believe that this large difference is caused by the 80 mol% SiO_2 composition exhibiting small plastic deformation.

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