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Hardness of silicate glasses: Atomic-scale origin of the mixed modifier effect

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ABSTRACT

The origin of the various manifestations of the mixed modifier effect in silicate glasses remains poorly understood. Here, based on molecular dynamics simulations, we investigate the origin of a negative deviation from linearity in the hardness of a series of mixed alkaline earth aluminosilicate glasses. The minimum of hardness is shown to arise from a maximum propensity for shear flow deformations in mixed compositions. We demonstrate that this anomalous behavior originates from the existence of local structural instabilities in mixed compositions arising from a mismatch between the modifiers and the rest of the silicate network. Overall, we suggest that the mixed modifier effect manifests itself as a competition between the thermodynamic driving force for structural relaxation and the kinetics thereof.

1. Introduction

Glasses comprising mixed modifiers (e.g., alkali or alkaline earth cations) often exhibit non-additive trends in their properties when one modifier is gradually replaced by another [1–7]—a behavior known as the "mixed-modifier effect." Although the mixed-alkali effect has been thoroughly addressed in previous studies [2,3], the mixed-alkaline-earth effect remains less studied, despite the importance of alkali-free glasses, e.g., for display applications [8].

Glasses comprising mixed modifiers can exhibit positive or negative deviations from linearity in their properties, including diffusivity, conductivity, glass transition temperature, molar volume, relaxation, or mechanical properties [1,2,4–6,9–13]. In particular, hardness, which characterizes a glass's resistance to permanent deformation, has been shown to be affected by the mixed modifier effect [1–3,9]. Although mixed-alkali glasses typically exhibit a positive deviation from linearity in their hardness [14], Yue et al. recently reported a negative deviation in the hardness of mixed alkaline earth aluminosilicate glasses when Ca are substituted by Mg cations [9]. This effect was attributed to an increase in the propensity for shear flow deformations upon loading in mixed compositions [9]. In contrast to these results, Zwanziger et al. reported a positive deviation in the hardness of a different series of mixed alkaline earth silicate glasses [1], which, in turn, was attributed to a decrease in the ability of the atoms to reorganize via shear flow. These different observations highlight the fact that the mixed modifier effect and its atomic origin remain largely unknown.

Here, based on molecular dynamics (MD) simulations of mixed alkaline earth aluminosilicate glasses, we investigate the origin of the mixed modifier effect and its propensity to increase or decrease hardness. The simulated glasses are found to exhibit a negative deviation from linearity in their hardness, which arises from an increased propensity for shear flow. We show that this behavior originates from the presence of local structural instabilities in mixed compositions, which act as a driving force for relaxation under load. Finally, we suggest that the contradictory observations (i.e., positive or negative deviations from linearity in hardness) can be rationalized in terms of a balance between the kinetics of atomic relaxation and its thermodynamic driving force.

2. Methodology

2.1. Preparation of the glasses

To establish our conclusions, we simulated a series of 17 mixed alkaline earth sodium aluminosilicate glasses $(CaO)_x(MgO)_{16-x}$

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Table 1
Compositions (in mol %) of the 17 mixed alkaline earth sodium aluminosilicate glasses simulated in this study.

Ca / (Ca + Mg)	CaO	MgO	Al_2O_3	SiO_2	Na_2O
0.0	0	16	12	60	12
0.0625	1	15	12	60	12
0.125	2	14	12	60	12
0.1875	3	13	12	60	12
0.25	4	12	12	60	12
0.3125	5	11	12	60	12
0.375	6	10	12	60	12
0.4375	7	9	12	60	12
0.5	8	8	12	60	12
0.5625	9	7	12	60	12
0.625	10	6	12	60	12
0.6875	11	5	12	60	12
0.75	12	4	12	60	12
0.8125	13	3	12	60	12
0.875	14	2	12	60	12
0.9375	15	1	12	60	12
1.0	16	0	12	60	12

$(Na_2O)_{12}(Al_2O_3)_{12}(SiO_2)_{60}$ with classical MD, using the LAMMPS package [15]. This series mimics that considered in the work of Kjeldsen et al. [9] (see the list of compositions in Table 1). The series of simulated glasses comprise 2990 atoms. To ensure that such size is large enough, a series of three glasses (with $x = 0$, 8, and 16%) were also simulated. For all the simulations, we relied on the well-established Pedone potential [16], as it has been shown to predict realistic mechanical properties for aluminosilicate glasses [16–18]. A cutoff distance of 8.0 Å was used. The Coulombic interactions were calculated via the damped shifted force model [19].

All the glasses were generated through the conventional melt-quench method [20–22] as follows. First, the atoms were randomly placed in a cubic box, while ensuring the absence of any unrealistic overlap. The system was then melted at 4000 K for 100 ps to ensure the loss of the memory of the initial positions. The liquids were subsequently quenched from 4000 K to 300 K with a cooling rate of 1 K/ps. Although the cooling rates typically used in MD simulations are significantly higher than those typically achieved experimentally, the structure of the formed glasses typically shows a good agreement with experiments [17,21,23–25]. After cooling, the obtained glasses were finally further relaxed for 1 ns at 300 K. The whole glass preparation process was performed within the *NPT* ensemble under zero pressure. For each composition, six independent glasses were generated for statistic average. In the following, all the presented data are averaged over those six replicas and their error bars are determined from the extent of statistical fluctuations. Fig. 1 shows a snapshot of the atomic structure of a slice of a mixed Ca-Mg ($x = 8\%$) aluminosilicate glass.

2.2. Hardness computation

The hardness of each glass was computed via the method introduced by Qomi et al. [26–30] and summarized in the following. First, all glasses were relaxed to zero temperature and pressure through an enthalpy minimization. Fifteen independent strain-controlled deformations (pure uniaxial tension/compression, pure shear, and combinations thereof) were then applied to the samples, by gradually varying the strain by increments of 10^{-4}. For each deformation, the yield point was identified from the 0.2% offset method [27]. The obtained shear and tensile stresses at the yield point were used to draw a Mohr's circle. The envelope of all the Mohr's circles allowed us to determine the failure limit of each sample, which was found to be well predicted by the Mohr-Coulomb failure criterion:

$$\tau = \sigma \tan(\varphi) + C \quad (1)$$

where τ is the failure shear stress for a given tensile stress σ, φ the friction angle, and C the cohesive strength. The hardness was then calculated as $H = 5.8\,C$ based finite-element results [31]. Note that the hardness values computed with this approach were shown to agree well with experimental data obtained at room temperature within the extent of the error bars [26–28]. More details about this method and its validation can be found in Refs. [26,28].

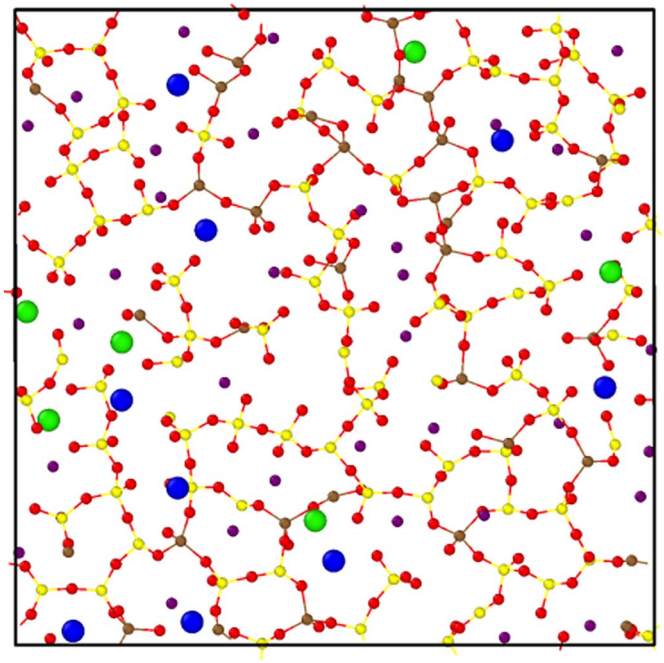

Fig. 1. Snapshot of the atomic structure of a slice of a mixed Ca-Mg aluminosilicate glass. Si, Al, Na, Ca, Mg, and O atoms are indicated in yellow, brown, violet, green, and blue, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2.3. Contribution of permanent densification to hardness

The hardness of oxide glasses can typically be limited by the appearance of permanent densification and/or shear flow under the indenter tip [2]. First, the propensity for permanent densification upon loading was assessed by subjecting the glasses to hydrostatic compressive pressures of 10 GPa and 20 GPa. The load was applied in the *NPT* ensemble for 1 ns, which was found to be sufficient for the volume and energy of the glasses to plateau. The densified glasses were subsequently relaxed to zero pressure for another 1 ns. The extent of load-induced permanent densification was then calculated as:

$$\frac{\Delta V}{V_i} = \frac{V_i - V_f}{V_i} \quad (2)$$

where V_i and V_f are the molar volume of the glass before and after the loading cycle, respectively.

2.4. Contribution of shear flow to hardness

Second, the propensity for shear flow deformations under load was determined by applying the following methodology. Each glass sample was subjected to a shear deformation by gradually increasing the shear strain by steps of 0.2%. At each step, the energy of the system was minimized and the mean square displacement (MSD) of the atoms recorded. The final shear strain was chosen as 40%, which was found to be sufficient for every glass to reach its yield point. We ensured that small variations in this value did not affect our conclusions. Ultimately, the system was relaxed to zero pressure. The shear flow deformations were estimated from the average final irreversible MSD of each atomic species, that is, after loading and unloading. Note that this MSD would