INTRODUCTION

The availability of thin, flexible, and damage-resistant glasses is a key requisite for many of today’s glass applications, including windshields, façade elements, or display covers for personal electronic devices. Brittleness and the high susceptibility of glasses to surface flaws result in catastrophic failure under load, with attainable practical strengths far below the theoretical limits. This problem has stimulated intensive research on the fundamental deformation modes in glasses and their implications for the generation of surface defects. At the same time, various methods are employed which enhance the practical strength of glasses. Among these, the most popular are to equip the glass product with a residual surface compressive stress layer through thermal or chemical post-processing. Chemically strengthened glasses are produced through diffusive ion exchange, which typically involves the immersion of an alkali-containing glass into a

Surface damage resistance and yielding of chemically strengthened silicate glasses: From normal indentation to scratch loading

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Abstract

We report on surface elasticity, plastic deformation and crack initiation of chemically strengthened soda-lime silicate and sodium aluminosilicate glasses during lateral indentation and scratch testing. Instrumented indentation using a normal indenter set-up corroborated previous findings on the effects of chemical strengthening on surface Young's modulus, hardness, and indentation cracking. Using lateral indentation in the elastic-plastic regime, we find a pronounced increase in the scratch hardness as a result of chemical strengthening, manifest in higher work of deformation required for creating the scratch groove. Thereby, the glass composition is found to play a stronger role than the absolute magnitude of surface compressive stress. Using a blunt conical stylus for instrumented scratch testing reveals three distinct modes of scratch-induced surface fracture, which occur during scratching or after unloading. Occasional micro-cracking caused by pre-existing surface flaws at low scratching load can be completely suppressed through chemical strengthening. The intrinsic defect resistance to microcracking is reduced as a result of ion stuffing, depending on the initial glass composition, whereas the resistance to abrasive yielding is enhanced by several hundred MPa.

KEYWORDS
abrasive wear, chemical strengthening, crack resistance, glass, hardness, indentation, mechanical properties, scratching
bath of molten salt at temperatures below the glass transition. During this process, the smaller alkali cations at the glass surface (e.g., Na\(^+\)) are replaced by larger cations from the salt bath (e.g., K\(^+\)). This leaves the sought-after surface compressive layer.\(^6\) In optimizing the process conditions (i.e., the salt bath (e.g., K\(^+\)). This leaves the sought-after surface glasses.\(^5,7\) Besides the many technological aspects of post-treatment, the specific glass composition and network topology were found to be important parameters for achieving efficient chemical strengthening.\(^8-10\) For example, very high levels of surface compressive stress are typically obtained in sodium aluminosilicate glasses.

Recent progress in the design of chemically strengthened glasses goes hand in hand with improved understanding of the initiation and growth of microscopic flaws at glass surfaces.\(^11\) Such understanding is often generated by examining the initiation of well-defined defects, for example, generated using sharp Vickers or Berkovich indenter tips\(^3\) or wedges.\(^12,13\) Also on chemically strengthened glasses, indentation deformation and cracking,\(^8,14-21\) scratch resistance,\(^21-24\) abrasive wear,\(^20\) and the response to impact load\(^16,17,25,26\) were extensively studied over the past years. However, sharp contact experiments such as underlying most of these studies represent rather harsh conditions, with local stress easily approaching the range of 10 GPa. In such cases, the intricate interplay of elastic-plastic deformation, yielding and crack formation is challenging to resolve. Lateral indentation using a blunt stylus was therefore considered as a means to experimentally study glass behavior at the very onset of surface yielding.\(^27\)

Here, we report on surface elasticity, plastic deformation, defect initiation, and surface fracture of chemically strengthened glasses observed during normal and lateral indentation experiments using sharp and blunt indenter tips. We consider soda-lime silicate and sodium aluminosilicate glasses as representatives for two fundamentally different types of glass, and explore their variations in the occurrence of various modes of surface defects during instrumented scratch testing.

**2 | MATERIALS AND METHODS**

**2.1 | Sample preparation**

Samples of a standard soda-lime silicate glass (Paul Marienfeld GmbH & Co. KG, denoted SLS) and a commercial sodium aluminosilicate glass (Schott AG, denoted AS) were used in this work. The as-received glass slides with a thickness of 1 mm (SLS) and 2 mm (AS), respectively, were cut into rectangular pieces of 25 × 25 mm\(^2\) and immersed in a molten KNO\(_3\) salt bath to induce Na\(^+\)/K\(^+\)-ion exchange (IOX). Two different ion exchange conditions were employed for the SLS and AS glasses, representing typical extremes for glass chemical strengthening: 10 h at 450°C for SLS (denoted SLS-IOX) and 6 h at 420°C for AS (with reference to,\(^28\) denoted AS-IOX). The obtained depth of layer DOL and surface compressive stress CS generated by the ion exchange process were evaluated after washing using a surface stress meter (FSM-6000LE, Luceo Co., Ltd.). Characteristic data of the ion exchange process are summarized in Table 1.

Stress relaxation was done by subsequent thermal treatment of the ion-exchanged glasses for 1 h at temperatures of approximately 0.95 \(T_g\). For this, the glass transition temperatures of SLS (\(T_g\) =567°C) and AS (\(T_g\) =615°C) were taken from the corresponding product data sheets. Salt baths were renewed after each ion exchange experiment in order to avoid contamination effects.

For reference, two series of mixed sodium-potassium silicate (SLS glass series) and aluminosilicate glasses (AS glass series) were prepared. Their nominal chemical compositions were selected based on the SLS and AS reference materials utilized for ion exchange (for simplification, minor components present in the commercial SLS and AS glasses were neglected). Starting from the corresponding end member, for each glass series, the total alkali molar content was fixed, but the Na\(_2\)O-to-K\(_2\)O molar ratio was varied in three steps per series. All glasses were synthesized from powder mixtures of high purity SiO\(_2\) (Carl Roth GmbH & Co. KG), Al\(_2\)O\(_3\) (Carl Roth GmbH & Co. KG), 4MgCO\(_3\)-Mg(OH\(_2\))\(_2\)-5H\(_2\)O (Merck KGaA), CaCO\(_3\) (Merck KGaA), Na\(_2\)CO\(_3\) (Carl Roth GmbH & Co. KG), K\(_2\)CO\(_3\) (Merck KGaA), and ZrO\(_2\) (ReaChim).

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**Table 1** Process conditions for the Na\(^+\)/K\(^+\)-ion exchange in the commercial soda-lime silicate (SLS) and aluminosilicate glasses (AS) and characteristic data of the compressive layers: ion exchange temperature \(T\), treatment time \(t\), surface compressive stress \(CS\), depth of layer \(DOL\), interdiffusion coefficient \(D\), and linear network dilation coefficient \(B\). The values of \(D\) were estimated via Equation (13) and values of \(B\) were calculated by means of Equation (11).

| Glass   | \(T\) (°C) | \(t\) (h) | \(CS\) (MPa) | DOL (µm) | \(D\) (cm\(^2\)/s) | \(B\) (10\(^{-3}\) [mol% K\(_2\)O]\(^{-1}\)) |
|---------|------------|-----------|--------------|----------|---------------------|--------------------------------------------|
| SLS     | —          | —         | —            | —        | —                   | 2.09                                       |
| SLS-IOX | 450        | 10        | 554          | 16.4     | 1.25 \(10^{-11}\)   | 0.50                                       |
| AS      | —          | —         | —            | —        | —                   | 2.06                                       |
| AS-IOX  | 420        | 6         | 891          | 45.4     | 1.59 \(10^{-10}\)   | 1.45                                       |
Batches of 150 g were melted in Pt crucibles, using a conventional muffle furnace. The compositions of the SLS glass series were melted for 3 h at 1450°C, whereas the aluminosilicate compositions required a higher melting temperature of 1650°C and an enhanced dwell time of 9 h. For casting, the temperature was further raised by about 20°C. As-cast glasses were transferred to a cooling furnace and annealed for 1 h at a temperature of 0.95 T_g, before cooling to room temperature at a rate of 2 K/min. For the subsequent chemical analysis and mechanical characterization, the glasses were cut into samples of about 25 × 25 mm^2 in size and 2 mm in thickness, and polished on both sides using fine-grained CeO_2.

The chemical compositions of all glasses were analyzed by means of energy dispersive X-ray spectrometry (EDX, Bruker XFlash 5010, Bruker Nano GmbH) after coating with a carbon layer of approximately 5 nm in thickness. For each glass, one spectrum was recorded for an accumulation live time of 500 s, using an incident beam with an electron energy of 15 keV. The normalized chemical compositions as determined by EDX are summarized in Table 2.

2.2 | Mechanical characterization

Elastic properties were determined by ultrasonic echography. Values of the shear modulus G, bulk modulus K, Young’s modulus E and Poisson’s ratio ν were calculated by means of the following equations:

\[
G = \rho c_T^2, \quad (1a)
\]
\[
K = \rho \left( c_L^2 - \frac{4}{3} c_T^2 \right), \quad (1b)
\]
\[
E = \rho \left[ \frac{3 c_L^2 - 4 c_T^2}{(c_L/c_T)^2 - 1} \right], \quad (1c)
\]
\[
\nu = \frac{c_T^2 - 2 c_T^2}{2 (c_L^2 - c_T^2)}, \quad (1d)
\]

where \(c_L\) and \(c_T\) are the longitudinal and transversal sound velocities, respectively, and \(\rho\) is the mass density as obtained with an Archimedes balance in distilled water (experimental error ±0.01 g/cm^3). Values of \(c_L\) and \(c_T\) were derived from the corresponding sound wave propagation times recorded with an accuracy of ±1 ns by piezoelectric transducers operating in the frequency range of 8 to 12 MHz (Echometer 1077, Karl Deutsch GmbH & Co. KG). The exact thickness of the polished glass samples was determined with an accuracy of ±2.5 μm using a micrometer screw.

The Vickers hardness \(H_V\) was investigated with a micro-hardness tester (Duramin-1, Struers GmbH). On each glass, 20 indents with a maximum load of 981 mN were created, using an indentation duration of 15 s. Values of \(H_V\) were calculated from the applied normal load \(P\) and the size of the residual hardness imprint, where \(d\) represents the average length of projected diagonals of the residual imprint. The resistance against the initiation of median-radial cracks was characterized by Vickers indentation. For this, indents were created with increasing normal load (ranging from 245.3 mN to 19.62 N) and the number of median-radial cracks appearing at the corners of the residual

| Glass          | R   | SiO_2 | Al_2O_3 | MgO | CaO | Na_2O | K_2O | Others |
|----------------|-----|-------|---------|-----|-----|-------|------|--------|
| As-melted glasses |     |       |         |     |     |       |      |        |
| SLS-Na         | 0.02| 74    | 1       | 3   | 10  | 12    | <1   | <1     |
| SLS-Na/K       | 0.33| 74    | 1       | 3   | 10  | 8     | 4    | <1     |
| SLS-K          | 0.98| 73    | 1       | 4   | 9   | <1    | 12   | <1     |
| AS-Na          | 0.18| 69    | 11      | 3   | —   | 13    | 3    | <1     |
| AS-Na/K        | 0.50| 71    | 9       | 4   | —   | 8     | 8    | <1     |
| AS-K           | 0.96| 68    | 12      | 4   | —   | <1    | 15   | <1     |
| SLS-IOX        | 0.01| 72    | 1       | 6   | 8   | 12    | <1   | <1     |
| SLS-IOX-A      | 0.84| 72    | 1       | 6   | 8   | 2     | 11   | <1     |
| AS             | 0.19| 68    | 11      | 5   | —   | 12    | 3    | 1      |
| AS-IOX         | 0.64| 68    | 11      | 6   | —   | 5     | 9    | 1      |
| AS-IOX-A       | 0.70| 68    | 11      | 6   | —   | 4     | 10   | 1      |
Vickers imprints was counted. On every glass, 25 indentations were performed per normal load. The probability of crack initiation PCI for each load increment was calculated based on the number of corners with median-radial cracks (count) divided by the total number of corners of all imprints (4 × 25). To determine the crack resistance CR, the values of PCI were plotted against P and fitted to a sigmoid function, whereby CR was defined as the load required to generate on average two median-radial cracks (i.e., PCI = 50%).

Instrumented indentation and scratch testing were carried out using a nanoindenter (G200, KLA Co.), equipped with a continuous stiffness measurement (CSM) unit and a lateral force measurement (LFM) option. Depending on the applied testing protocol, a three-sided Berkovich diamond tip and a conical diamond indenter with a tip angle of 60° and an effective tip radius of 5.23 µm were employed (Syntone-MDP Inc.). The area function of the indenter tips and the instrument's frame compliance were calibrated prior to the first experiments on a fused silica reference glass (Corning Code 7980, Corning Inc.), according to the method of Oliver and Pharr. Indentation experiments were carried out in CSM mode with the Berkovich indenter. The strain-rate sensitivity of Young's modulus and Poisson's ratio, respectively, of the Berkovich diamond tip was determined from constant-thermal drift rates of <0.05 nm/s.

The scratch hardness \( H_S \) was determined from constant-normal load up to a maximum of 400 µm. Scratch testing was carried out on every glass sample at three different normal loads of 350; 600 and 800 nm. The values of \( H_S \) were then derived from the slope of a linear fit of the work of deformation \( W_S \) during scratching (defined as the integral of \( F_d \) d\( L_S \), averaged over ten scratch tests per normal load) to the volume of the scratch groove \( V_S \) (Figure S1B),

\[
H_S = \frac{dW_S}{dV_S},
\]

with

\[
V_S = \int A_{\text{tan}} dL_S = \int \frac{\sqrt{3}h^2}{2\tan \beta} dL_S.
\]

Here, \( A_{\text{tan}} \) is the projected tangential area of the indenter tip in the scratching direction; \( \beta \) denotes the contact angle between the indenter tip and the glass surface, which is 12.95° for a Berkovich diamond indenter in edge-forward orientation. To ensure a stationary scratch response, the above analysis of \( V_S \) and \( W_S \) was limited to a section of 100 µm, neglecting the first and last 50 µm of each scratch.

For blunt testing, ramp-load scratching experiments were performed using the conical diamond indenter mentioned above. In accordance with a previous report, the indenter tip was moved across a distance of 800 µm while monotonically increasing the normal load up to a maximum of 400 µm. Maintaining the scratching speed at 50 µm/s, this resulted in a constant loading rate of 25 mN/s throughout the experiments. Longitudinal profiles of the permanent scratch grooves were obtained directly after scratching from post-scans of the scratch track under a constant normal load of 50 µm. The residual scratch patterns were further analyzed by widefield confocal microscopy (Smartproof 5, Zeiss AG). All indentation experiments and scratch tests were carried out in laboratory air at ambient temperatures of 25 ± 3°C and with thermal drift rates of <0.05 nm/s.

### 3 Results and Discussion

#### 3.1 Properties of bulk reference glasses

The mechanical properties of the glasses investigated in this work are summarized in Table 3. In the following section
TABLE 3 Mechanical properties of the investigated silicate and aluminosilicate glasses: shear modulus $G$, bulk modulus $K$, Poisson's ratio $\nu$, Young's modulus $E$, hardness $H$, strain-rate sensitivity $m$, scratch hardness $H_s$, Vickers hardness $H_V$, and crack resistance $CR$. The parameter $R$ represents the $[K_2O]/([Na_2O] + [K_2O])$ molar ratio (see also Table 2).

| Glass          | $R$  | $G$   | $K$    | $\nu$ | $E$  | $E$  | $H$ | $m$    | $H_s$ | $H_v$ | $CR$ |
|---------------|------|-------|--------|-------|------|------|-----|--------|------|-------|------|
| As-melted glasses |      |       |        |       |      |      |     |        |      |       |      |
| SLS-Na        | 0.02 | 29.9  | 44.5   | 0.226 | 73.2 | 76.8 | 6.73| 0.0191 | 6.9  | 5.3   | 0.99 |
| SLS-Na/K      | 0.33 | 29.1  | 43.5   | 0.227 | 71.4 | 75.5 | 7.00| 0.0186 | 7.1  | 5.9   | 0.61 |
| SLS-K         | 0.98 | 26.2  | 40.2   | 0.232 | 64.7 | 67.6 | 6.44| 0.0195 | 7.0  | 5.2   | 0.99 |
| AS-Na         | 0.18 | 30.4  | 42.8   | 0.212 | 73.8 | 73.6 | 6.98| 0.0216 | 6.7  | 6.3   | 5.00 |
| AS-Na/K       | 0.50 | 29.2  | 41.7   | 0.216 | 71.1 | 71.2 | 6.96| 0.0199 | 6.2  | 6.2   | 4.91 |
| AS-K          | 0.96 | 26.8  | 39.1   | 0.222 | 65.4 | 67.5 | 7.05| 0.0197 | 6.4  | 6.3   | 6.91 |
| Ion-exchanged glasses |      |       |        |       |      |      |     |        |      |       |      |
| SLS           | 0.01 | 29.8  | 46.4   | 0.236 | 73.6 | 76.7 | 6.83| 0.0170 | 7.5  | 4.9   | 1.01 |
| SLS-IOX       | 0.84 | —     | —      | —     | —    | 73.6 | 76.7 | 6.83  | 0.0170 | 7.5  | 4.9   | 1.01 |
| SLS-IOX-A     | 0.84 | —     | —      | —     | —    | 73.6 | 76.7 | 6.83  | 0.0170 | 7.5  | 4.9   | 1.01 |
| AS            | 0.19 | 30.4  | 43.7   | 0.217 | 74.1 | 73.9 | 6.91| 0.0238 | 7.1  | 6.2   | 9.88 |
| AS-IOX        | 0.64 | —     | —      | —     | —    | 76.4 | 7.93 | 7.05  | 0.0159 | 7.7  | 6.9   | —   |
| AS-IOX-A      | 0.70 | —     | —      | —     | —    | 74.3 | 7.10 | 6.95  | 0.0206 | 6.4  | 6.5   | 6.95 |
| Experimental error | — | ± 0.2 | ± 0.7 | ± 0.006 | ± 1.2 | ± 0.2 | ± 0.3 | — | ± 0.1 | ± 0.2 | — |

$^a$Values of $E$ as determined from ultrasonic echography.

$^b$Values of $E$ as determined through nanoindentation. For the ion-exchanged and annealed silicate and aluminosilicate glasses (where no Poisson's ratio was determined by ultrasonic echography), the values of $\nu = 0.236$ (SLS) and 0.217 (AS) of the as-received glasses were used to calculate Young's modulus from the reduced elastic modulus $E_r$, according to Equation (3).

(Section 3.1), we first discuss the effect of varying the alkali molar ratio $R = [K_2O]/([Na_2O] + [K_2O])$ on the mechanical properties of the bulk sodium-potassium silicate and aluminosilicate reference glasses. This is to facilitate the later discussion of the mechanical property variations observed in the ion-exchanged SLS and AS glasses in terms of the individual effects of the surface compressive stress and diffusion-induced alterations in chemical composition (Sections 3.2 and 3.3).

The dependence of the elastic properties of bulk SLS and AS glasses on $R$ is depicted in Figure S2. The experimentally determined values of $G$, $K$, $E$, and $\nu$ obtained for the as-melted Na$_2$O-rich compositions (SLS-Na: $R = 0.02$ and AS-Na: $R = 0.18$) are in good agreement with the experimental results from the commercial SLS ($R = 0.01$) and AS glasses ($R = 0.19$) used for ion exchange (Table 3), as well as with the values tabulated in the corresponding data sheets. Minor deviations are attributed to slight variations between the chemical compositions of the commercial and laboratory-melted samples (Table 2). In the series of mixed sodium-potassium silicate glasses, a monotonic decrease of $G$, $K$, and $E$ is seen with increasing molar ratio $R$. $\nu$ increases slightly when Na$_2$O is replaced by K$_2$O. Similar trends occur in the series of mixed sodium-potassium aluminosilicate glasses: the substitution of Na$_2$O by K$_2$O results in a reduction of $G$, $K$, and $E$ as well as in a slight increase of $\nu$. These trends correspond very well to previous reports on mixed alkali silicate$^{41-45}$ or aluminosilicate glasses$^{45,46}$ The compositional variations in the elastic properties of the bulk SLS and AS glasses investigated here are roughly proportional to $R$ (with only three datapoints per glass series, discussing any mixed alkali effect is outside the scope of the present report).

Despite the marked differences in chemical composition (the silicate glasses contain ~$9$ mol% CaO and less than 1 mol% Al$_2$O$_3$, whereas the aluminosilicate glasses are free of CaO but contain about 9 mol% of Al$_2$O$_3$, see Table 2), the AS and SLS glass types exhibit similar values of $G$, $K$, and $E$ for equal values of $R$. However, the as-melted aluminosilicate glasses exhibit consistently lower $\nu$. The latter is a result of differences in the average network connectivity between the two glass systems, whereas the similarities in $G$, $K$, and $E$ result from similar changes in bond energy density. Using the semi-empirical model of Makishima and Mackenzie$^{47}$ (MM), Young's modulus of a glass is approximated from the volume density of bond energy $<U_0/V_0>$ and the atomic packing density $C_g$:

$$E = 2C_g \frac{U_0}{V_0},$$

where $<U_0/V_0>$ is the average atomic bond energy $U_0$ per the effective molar volume $V_0$ of the glass. $V_0$ is obtained from the molar mass $M_i$ of every single glass constituent, weighted by its molar fraction $f_i$, and the mass density of the glass.$^{48}$
\[ V_0 = \frac{\sum i f_i M_i}{\rho} \] (8)

The parameter \( U_0 \) is derived from the weighted average of the molar dissociation enthalpy \( \Delta H_{ai} \) of each glass component. Values of \( \Delta H_{ai} \) are calculated from the molar heats of formation \( \Delta H_i \) of the corresponding oxides \( A_xO_y \) in their crystalline state, and the respective atoms in their gaseous states, using the equation:

\[ \Delta H_{ai} = x\Delta H(A, \text{gas}) + y\Delta H(O, \text{gas}) - \Delta H(A_iO_y, \text{crystal}), \] (9)

using the values of \( \Delta H \) listed by Lide. Finally, the atomic packing density is estimated from the values of \( \Delta H_{ai} \) listed by Lide. (9)

\[ C_g = \frac{\sum i f_i V_i}{\sum i f_i M_i}. \] (10)

Here, \( V_i = 4/3 \pi N (x r_A^3 + y r_O^3) \) represents the theoretical molar volume occupied by the ions of \( A_xO_y \). \( N \) is the Avogadro constant and \( r_A \) and \( r_O \) are the ionic radii of the involved cations and oxygen \((r_O = 135 \text{ pm})\), respectively. Values of \( V_i \) were calculated using the effective ionic radii provided by Shannon and Lide.50 Finally, the atomic packing density is estimated from the values of \( \Delta H_{ai} \) listed by Lide.50

The observed increase of \( v \) with increasing molar ratio \( R \) may originate from the parallel increase of \( C_g \), upon progressive substitution of \( Na_2O \) by \( K_2O \). The slight offset in Poisson’s ratio between the series of mixed sodium-potassium silicate and aluminosilicate glasses may further reflect the underlying differences in network dimensionality and atomic packing efficiency between these two glass systems. Due to the presence of large amounts of network-forming \( Al^{14+} \) species (Table 2), the aluminosilicate glasses exhibit a higher degree of crosslinking as compared to the silicate glasses.

Using Equation (7), Young’s modulus of the as-melted \( Na_2O \)-rich silicate and aluminosilicate glasses was estimated as 67.1 GPa (SLS-Na: \( R = 0.02 \)) and 65.3 GPa (AS-Na: \( R = 0.18 \)), respectively (Table 4). In comparison with the experimental results obtained from ultrasonic echography (Table 3), the MM model clearly underestimates the actual values of Young’s modulus by about 6.1 GPa (SLS-Na: \( R = 0.02 \)) and 8.6 GPa (AS-Na: \( R = 0.18 \)), respectively. Over the past years, several potential explanations have been proposed as the origin of such a discrepancy. Even though the approach of MM fails in accurately predicting Young’s modulus of the mixed sodium-potassium silicate and aluminosilicate glasses, it properly reproduces the dependence of \( E \) on the molar ratio \( R \) for both glass series. This allows for a qualitative assessment of the individual factors responsible for the compositional effects, that is, the molar volume and molar dissociation enthalpy. The latter is decreasing significantly when \( Na_2O \) \( \Delta H_{ai} \) replaced by \( K_2O \) \( \Delta H_{ai} \). Increasing the molar ratio \( R \) consequently results in a progressive reduction of \( U_0 \). This effect, in combination with the above-mentioned parallel increase of \( V_i \), causes a substantial drop of \( \Delta H_{ai} \) (Table 4), which in turn causes a gradual reduction of \( E \) (Table 4; experimentally verified through ultrasonic echography, see Figure S2).

| Glass | \( R \) | \( \rho \) (g/cm\(^3\)) | \( V_0 \) (cm\(^3\)/mol) | \( C_g \) | \( <U/V_0> \) (kJ/cm\(^3\)) | \( E \) (GPa) | \( B \) (10\(^{-3}\) [mol% \( K_2O \)]) |
|-------|-------|-----------------|-----------------|------|-----------------|------|-----------------|
| SLS-Na | 0.02 | 2.45 | 23.96 | 0.489 | 68.5 | 67.1 | 2.06 |
| SLS-Na/K | 0.33 | 2.45 | 24.45 | 0.501 | 66.7 | 66.8 | 2.02 |
| SLS-K | 0.98 | 2.45 | 25.67 | 0.518 | 63.4 | 65.7 | 1.92 |
| AS-Na | 0.18 | 2.44 | 27.22 | 0.487 | 67.0 | 65.3 | 2.04 |
| AS-Na/K | 0.50 | 2.43 | 27.56 | 0.499 | 64.7 | 64.5 | 2.02 |
| AS-K | 0.96 | 2.42 | 29.15 | 0.512 | 62.3 | 63.8 | 1.91 |
Given the fact that the elastic constants $G$, $K$, and $E$ are interrelated by $E = 2G(1 + \nu) = 3K(1 - 2\nu)$, and with regard to the marginal changes in $\nu$, it is reasonable to apply the same arguments to the dependence of $G$ and $K$ on $R$, too.

As compared to their elastic properties, the differences in indentation hardness and scratch behavior are more pronounced between the bulk sodium-potassium silicate and aluminosilicate glasses (see Figure S3). Young's modulus as determined through nanoindentation is in good agreement with the results from ultrasonic echography (Table 3), thus providing confirmation of the observed compositional trends.\(^{71}\) For indentation hardness, a mixed alkali effect is observed. Increasing the $K_2O$ content at the expense of $Na_2O$ initially leads to a slight increase of $H$ in the series of mixed sodium-potassium silicate glasses, from 6.73 GPa ($R = 0.02$) to 7.00 GPa ($R = 0.33$). This is followed by decrease of $H$ down to 6.44 GPa when $R = 0.98$. In the aluminosilicate system, the values of $H$ remain unaffected by the molar ratio $R$ within the experimental uncertainty of the employed nanoindentation set-up. To validate these observations, complementary Vickers microindentation experiments were performed (Table 3). Even though the absolute values of $H$ and $H_v$ may not coincide (due to the differences in the hardness evaluation between instrumented indentation and Vickers microhardness testing\(^3\)), qualitatively equivalent compositional trends are usually obtained for $H$ and $H_v$. \(^{48,63,72-74}\) In the series of mixed sodium-potassium silicate glasses, $H_v$ increases first from 5.3 GPa ($R = 0.02$) to 5.9 GPa ($R = 0.33$), but then decreases back to 5.2 GPa for the $K_2O$-rich glass ($R = 0.98$). In the aluminosilicate system, $H_v$ varies only slightly from 6.3 GPa ($R = 0.18$) to 6.2 GPa ($R = 0.50$) and 6.3 GPa ($R = 0.96$), confirming the weaker – if any – dependence of hardness on molar ratio $R$.

The same trends also occur in the resistance to scratching. The as-melted sodium-potassium aluminosilicate glass with equal amounts of $Na_2O$ and $K_2O$ ($R = 0.50$) exhibits a notably lower scratch resistance ($H_S = 6.2$ GPa) in comparison to the $Na_2O$-rich ($H_S = 6.7$ GPa for AS-Na: $R = 0.50$) and $K_2O$-rich counterparts ($H_S = 6.4$ GPa for AS-K: $R = 0.96$). An inverse, but significantly less pronounced trend is seen for the scratch hardness in the series of mixed sodium-potassium silicate glasses (see Figure S3). Similar moderate deviations from linearity have already been reported in several studies on the indentation response of mixed alkali silicate\(^{12,45,75}\) or aluminosilicate glasses.\(^{45,46}\) In most of these studies, the hardness as well as associated properties (e.g., crack resistance or indentation fracture toughness) exhibited a maximum divergence from linearity for $R = 0.5$. Our present findings on the compositional dependence of indentation and scratch hardness corroborate these observations for the series of mixed sodium-potassium silicate and aluminosilicate glasses. A more detailed consideration of the bulk reference glasses, however, is outside of the scope of the present study.

Compositional variations in the creep resistance were analyzed in a nanoindentation strain-jump test (see Section 2.2 for details). The values of strain-rate sensitivity for the as-melted sodium-potassium silicate and aluminosilicate glasses are located within the typical range of strain-rate sensitivities reported for silicate glasses.\(^{35,48,67,73,76,77}\) Modifying the molar ratio $R$ results in almost negligible changes of $m$, with a maximum difference of about 0.001 (SLS series) and 0.002 (AS series), respectively. This result compares very well to the extent of strain-rate sensitivity alterations reported for a series of metaphosphate glasses containing pairs of different alkaline species ($Mg^{2+}$, $Ca^{2+}$, and $Sr^{2+}$) in varying molar ratios.\(^{35,78}\) Substantially larger variations in strain-rate sensitivity are actually not expected in the current series of mixed sodium-potassium silicate and aluminosilicate glasses,\(^35\) since the partial or full replacement of $Na^+$ by $K^+$ affects predominantly the short-range order around the network modifying cation, whereas the intermediate- to long-range structural order remains mostly unaffected.\(^{57,58,79}\)

The indentation crack resistance, defined as the load at which on average two median-radial cracks per Vickers indenter form during indentation testing, is also shown in Figure S2. Values of crack resistance estimated for the as-melted sodium-potassium silicate glasses are in line with previous reports on comparable glass compositions.\(^{38,73,80,81}\) Only minor changes in $CR$ were found when varying $R$. Given the experimental uncertainty of the employed method\(^{67,82,83}\) along with the sparse results in almost negligible changes of $m$, the trend within each glass series is not clear. Between both glass series, the difference is about one order of magnitude. This is in accordance with previous observations of a consistently higher defect resistance of aluminosilicate glasses as compared to conventional soda-lime silicates.\(^{65,84-88}\)

### 3.2 Stress build-up in ion-exchanged silicate and aluminosilicate glasses

Using the information on the properties of the as-melted mixed sodium-potassium silicate and aluminosilicate glasses, we now consider the effect of a $Na^+/K^+$-ion exchange on the mechanical performance of the commercial soda-lime silicate and aluminosilicate glasses during normal indentation and scratching using sharp or blunt indenter tips. Data on surface compressive stress $CS$, depth of layer $DOL$ and surface molar ratio $R$ of the chemically strengthened glasses are summarized in Table 1. The observed difference in the magnitude of surface compressive stress between the SLS and AS glasses is caused by the difference in network dilation.\(^{89}\) The stuffing process forces the $K^+$ ions into network sites which exhibit a local environment in-between the coordination environments of $Na^+$ and of $K^+$ in the compositionally equivalent as-melted glass.\(^{57,58,79}\) The resulting stress profile (in the absence of stress relaxation) has been expressed as follows:\(^{90}\)
\[ \sigma(z) = \frac{BE}{1 - \nu} \left[ C(z) - C_{\text{avr}} \right], \quad (11) \]

where \( C(z) \) and \( C_{\text{avr}} \) are the local concentration of the invading alkali cation at a distance \( z \) from the glass surface and its average concentration inside the glass, respectively, and \( \sigma(z) \) is the magnitude of compressive stress as a function of \( z \). The parameter \( B \) is the linear network dilation coefficient (Cooper coefficient). It represents the amount of linear elastic strain accommodated by the glass per unit change in alkali concentration.\(^9\)

In a simple analogy to the thermal expansion coefficient, it can be calculated from\(^9\)

\[ B = \frac{1}{3V_0} \frac{\partial V_0}{\partial C}. \quad (12) \]

Values of \( B \) for the as-melted mixed sodium-potassium silicate and aluminosilicate glasses investigated in the current study were extracted from the slope of the linear regression of \( V_0 \) over the \( \text{K}_2\text{O} \) concentration, \( \partial V_0/\partial C \) (Figure 1A), normalized to \( V_0 \) (Table 4), according to Equation (12). The monotonic increase in molar volume with increasing \( \text{K}_2\text{O} \) concentration in the series of mixed sodium-potassium silicate and aluminosilicate glasses has already been discussed in Section 3.1. Linear regression applied to the data presented in Figure 1A yields slopes of 0.148 cm\(^3\)/(mol mol% \( \text{K}_2\text{O} \)) for the mixed sodium-potassium silicate and aluminosilicate glasses, respectively. Dividing \( \partial V_0/\partial C \) by a factor of 3 \( V_0 \) provides values for \( B \) of 2.06 \( \times \) \( 10^{-3} \) (mol% \( \text{K}_2\text{O} \))\(^{-1} \) (SLS-Na: \( R = 0.02 \)) and 2.04 \( \times \) \( 10^{-3} \) (mol% \( \text{K}_2\text{O} \))\(^{-1} \) (AS-Na: \( R = 0.18 \)), respectively, for the as-melted \( \text{Na}_2\text{O} \)-rich compositions mimicking the respective commercial SLS and AS glasses used for ion exchange. In both glass series, a slight decrease of \( B \) with increasing molar ratio \( R \) was noticed (Table 4).

The values of \( B \) for the ion-exchanged glasses were estimated via Equation (11), using the measured values of \( E \) and \( \nu \) from the as-received SLS and AS glass samples (Table 3). For \( C(z) \) and \( C_{\text{avr}} \), we consider the \( \text{K}_2\text{O} \) concentration as analyzed by EDX before and after ion exchange, respectively (Table 2). The results of these calculations are summarized in Table 1. A direct comparison of these data reveals a marked offset between the as-melted and ion-exchanged glasses (Figure 1B). This discrepancy is commonly referred-to as the network dilation anomaly and illustrates the mismatch between the theoretically attainable values of \( CS \), as predicted by Equation (11) using the values of \( B \) from Equation (12), and the magnitude of \( CS \) induced by ion exchange.\(^9\) For comparison, a surface compressive stress of 554 MPa was realized in the ion-exchanged SLS glass specimen (SLS-IOX), even though the theoretical limit is roughly 3.7 times higher (~2.1 GPa). Much larger fractions of the theoretically accessible surface compressive stress were achieved in the ion-exchanged AS glass (891 MPa in AS-IOX, as compared to the predicted value of ~1.2 GPa). The latter finding is well-supported by literature.\(^10,89,94-97\) Nevertheless, we need to emphasize that the origin of the network dilation anomaly is still not fully resolved. Based on molecular dynamics simulations, it has been suggested that the effect arises from the earlier mentioned unique local environment around the \( \text{K}^+ \) ions.\(^9,57,89\)

### 3.3 | Chemically strengthened silicate and aluminosilicate glasses during normal indentation testing

During chemical strengthening of glasses, a gradient in chemical composition is generated at the glass surface, also leading to depth-dependent mechanical properties. In the present case, we disregard this aspect by assuming a constant...
K$_2$O concentration and a flat stress profile within the top-most surface layer of the ion-exchanged glasses. The validity of this approximation is considered in Figure 2 for the ion-exchanged SLS glass (SLS-IOX: $R = 0.84$, $CS = 554$ MPa, $DOL = 16.4$ µm). With the information on the stress distribution and the duration of the ion exchange process $t$, an interdiffusion coefficient $D$ of $1.25 \times 10^{-11}$ cm$^2$/s was estimated (Table 1),

$$z = \sqrt{6Dt},$$

(13)

where $z$ is equal to the $DOL$ as derived from stress optical analysis. The corresponding concentration profile of K$_2$O (Figure 2) is then obtained through

$$C(z) = C_s \cdot \text{erfc} \left( \frac{z}{2\sqrt{Dt}} \right),$$

(14)

where $C_s$ is the concentration of the invading alkali cation at the glass surface as analyzed by EDX, that is, $C_s = C(z = 0)$ (Table 2). Within the first 2 µm of the ion-exchanged surface layer (corresponding to the depth range of the present indentation experiments) the magnitude of compressive stress is decreasing by about 46 MPa and the K$_2$O concentration, as predicted by Equation (14), changes by about 1.94 mol% (from $C(z = 0) = 11.59$ mol% to $C(z = 2$ µm) = 9.65 mol%). The relative extent of this effect is even smaller for the ion-exchanged AS glass (AS-IOX: $R = 0.64$, $CS = 891$ MPa, $DOL = 45.4$ µm): here, the K$_2$O concentration decreases only marginally by about 0.56 mol% (from $C(z = 0) = 9.24$ mol% to $C(z = 2$ µm) = 8.68 mol%), and the compressive stress decreases by about 57 MPa.

Depth-resolved instrumented indentation testing (CSM mode) was used to probe the gradient in elastic properties of the ion-exchanged layers on AS and SLS glasses (see Section 2.2 for details). Results for $E$ were derived from the experimentally determined values of $E_n$ according to Equation (3). However, this approach normally requires a prior knowledge on the Poisson’s ratio of the material tested. We decided to employ the values of Poisson’s ratio as obtained from the pristine glasses by ultrasonic echography (SLS: $v = 0.236$ and AS: $v = 0.217$, Table 3) also for the evaluation of the chemically strengthened and thermally relaxed glasses, respectively. Considering the compositional dependence of Poisson’s ratio, as observed on the as-melted mixed sodium-potassium silicate and aluminosilicate glasses (see Figure S1), we suppose that the error introduced by this approach is negligible. Depth profiles of Young’s modulus and hardness for the commercial soda-lime silicate and aluminosilicate glasses, in the as-received state (SLS and AS), after Na$^+$/K$^+$-ion exchange (SLS-IOX and AS-IOX) and following a thermal treatment for 1 h at a temperature of approximately 0.95 $T_g$ (SLS-IOX-A and AS-IOX-A), respectively, are provided in Figure S4. Mean values of $E$ and $H$ are summarized in Table 3. In each experiment, a mild increase of $E$ and $H$ with increasing penetration depth was seen for the first ~200 nm, related to tip imperfections and contact inhomogeneity. At higher penetration depth, $E$ and $H$ stay flat down to the prescribed depth limit of 2 µm. This observation supports our previous approximation that gradients in the surface properties of the chemically strengthened soda-lime silicate and aluminosilicate glasses can be neglected within the depth-range of the present indentation experiments (Figure 2). As a result of ion exchange, the mean value of $E$ determined on the surface of the commercial SLS glass sample was raised slightly from 76.7 GPa (SLS: $R = 0.01$) to 78.3 GPa (SLS-IOX: $R = 0.84$) (see Figure S4A and Table 3). Simultaneously, the hardness increased from 6.83 GPa (SLS) to 7.41 GPa.

**FIGURE 2** Prediction of surface modifications in SLS glass after Na$^+$/K$^+$-ion exchange for 10 h at 450°C (SLS-IOX): (left) compressive stress $CS$ as a function of distance from the glass surface $z$ and (right) variation of the K$_2$O concentration with $z$, as calculated by means of Equation (14). The insets drawings are shown at scale to illustrate the displacement ranges $h$ probed by instrumented indentation (2 µm) and constant load scratch testing (~800 nm), respectively (using a Berkovich indenter), as well as ramp-load scratch testing (~4 µm, using a conical indenter with a tip angle of 60° and an effective tip radius of 5.23 µm) (from left to right) [Color figure can be viewed at wileyonlinelibrary.com]
After annealing (SLS-IOX-A: \( R = 0.84 \)), Young's modulus returned to a value of about 75.4 GPa, which is below the value of the pristine SLS glass. The hardness recovered a value of 6.98 GPa, above that of the pristine SLS glass. The latter observations are in agreement with the variation in the surface molar ratio of \( R = 0.01 \) (SLS) to \( R = 0.84 \) (SLS-IOX-A); they follow the compositional trends of \( E \) and \( H \) within the series of mixed sodium-potassium silicate glasses (see Figure S1A and Figure S2A). Similar trends were found for the commercial AS glass (see Figure S4B and Table 3). Here, chemical strengthening caused an increase of \( E \) from 73.9 GPa (AS: \( R = 0.19 \)) to 76.4 GPa (AS-IOX: \( R = 0.64 \)). In parallel, the hardness was enhanced from 6.91 GPa (AS) to 7.93 GPa (AS-IOX). Annealing the chemically strengthened aluminosilicate glass resulted in the expected recovery of \( E \) and \( H \). But opposite to the relaxed soda-lime silicate glass, Young's modulus and hardness of the relaxed aluminosilicate glass (AS-IOX-A: \( R = 0.70 \)) remained slightly above the values of the pristine AS glass, with mean values for \( E \) of 74.3 GPa and for \( H \) of 7.10 GPa. The observed trends for the chemically strengthened SLS and AS glasses are consistent with earlier studies. The \( K^+ \) ions replacing \( Na^+ \) during the ion exchange process are stuffed into the glass network and yield a surface layer with a packing density exceeding that of the compositionally equivalent as-melted glass. With regard to the MM model and the preceding discussion in Section 3.1, the more efficient packing (larger \( C_g \)) in the compressive layer is supposed to balance the simultaneous decrease in the molar dissociation enthalpy arising from the substitution of \( Na_2O \) (\( \Delta H_{ai} = 878 \text{ kJ/mol} \)) by \( K_2O \) (\( \Delta H_{ai} = 789 \text{ kJ/mol} \)), with the result of an increasing \( E \) in the chemically strengthened glasses. A similar argument can be used for understanding the changes in hardness. The exchange of \( Na^+ \) by \( K^+ \) is expected to promote shear flow, given the fact that a network modifying cation with higher bond strength is replaced by one with lower bond strength (and higher polarizability). However, the enhanced susceptibility to shear flow in the ion-exchanged glasses appears to be fully compensated by the parallel creation of a densely-packed surface layer which, in turn, restricts further compaction of the material during indentation. In combination with the aforementioned increase of \( E \), this gives rise to the observed increase of \( H \). The results obtained for \( H_V \) from Vickers indentation testing corroborate these findings (Table 3).

Aside hardness, chemical strengthening also causes significant changes in crack resistance. Post mortem optical inspection of a representative residual Vickers hardness imprint on the as-received SLS glass sample (SLS, Figure 3A) reveals the formation of a complex crack pattern typical for so-called “normal glasses”, where shear flow

![Figure 3](https://wileyonlinelibrary.com)
prevails. In addition, numerous secondary radial cracks emanating from the edges of the Vickers imprint are seen, along with several edge cracks near the indentation mark. As a result of chemical strengthening, the extent of median-radial cracking (SLS-IOX, Figure 3B) is significantly reduced, presumably because the compressive layer counteracts the stresses responsible for crack nucleation in the indentation test. The crack resistance thereby increased from 1.0 N (SLS) to 6.9 N (SLS-IOX) (Table 3). At the same time, the propensity for lateral cracking and chipping is enhanced. Thermal treatment (pre-indentation) reverts all these effects (SLS-IOX-A, Figure 3C), The general features of the crack patterns on the as-received (AS, Figure 3D) and relaxed aluminosilicate glasses (AS-IOX-A, Figure 3F) do not markedly deviate from the crack patterns on the corresponding soda-lime silicate glasses. Obvious differences were identified only in the load threshold for indentation cracking between the commercial soda-lime silicate and aluminosilicate glasses (Table 3) and the mean length of the median-radial cracks. In the chemically strengthened aluminosilicate glass (AS-IOX, Figure 3E), the median-radial cracks are completely suppressed for loads up to 19.62 N (which was the load limit of the employed Vickers micro-hardness tester).

3.4 Lateral indentation testing on chemically strengthened silicate and aluminosilicate glasses

Experimental results from the constant load scratch tests on the commercial soda-lime silicate and aluminosilicate glasses are summarized in Table 3. Scratch testing was performed for moderate normal loads from 18 mN to 91 mN, corresponding to a narrow displacement range of 350–800 nm (see Section 2.2 for details). By this, we may safely exclude the influence of tip imperfections on the scratch response, while remaining within the topmost surface layer (where the K+ concentration and compressive stress can be approximated as constant (mean) values, see Figure 2 in Section 3.3). On first view, the variation in scratch hardness induced by chemical strengthening appears to follow the earlier discussed trends in Young’s modulus and indentation hardness. However, distinct deviations are seen in the relative changes of scratch hardness. Chemical strengthening of the commercial soda-lime silicate glass resulted in an increase of $H_S$ from 7.5 GPa (SLS) to 8.3 GPa (SLS-IOX). A smaller variation was obtained for the scratch hardness of the chemically strengthened aluminosilicate glass, despite the comparably higher level of surface compressive stress: $H_S$ increased from 7.1 GPa (AS) to 7.7 GPa (AS-IOX). This observation can be understood on the basis of glass composition. The mixed sodium-potassium silicate glasses (unlike the mixed sodium-potassium aluminosilicate glasses) exhibit a pronounced increase of $H_S$ as a function of $R$ (see Figure S2A). In combination with the additional, positive effects of ion stuffing (enhanced atomic packing density in the ion-exchanged surface layer), an increase in $H_S$ by about 0.8 GPa (SLS-IOX) is achieved in chemically strengthened soda-lime silicate glass. The decrease in $H_S$ with increasing $R$ in mixed sodium-potassium aluminosilicate glasses (see Figure S2B) counteracts the advantages of ion stuffing, thereby limiting the overall increase in $H_S$ for the chemically strengthened aluminosilicate glass to about 0.6 GPa (AS-IOX).

Ramp-load scratch tests were performed using a conical indenter. In comparison to the sharp Berkovich stylus, such a blunt tip provides considerably lower contact stress. This enables the evaluation of subtle changes in the lateral force response during the rate-controlled scratching experiment. Furthermore, it avoids issues associated with the orientation of the indenter tip relative to the scratching direction. Examples of ramp-load scratch tests on the commercial soda-lime silicate glasses in the as-received state and after chemical strengthening, respectively, are presented in Figure 4, together with images of the resulting scratch morphologies. Postmortem optical inspection of the residual scratch groove on the as-received soda-lime silicate glass (SLS, Figure 4A) reveals notable variations in the scratching behavior with increasing load level. The three characteristic scratch regimes which are typical for glasses are clearly visible: at the early stage of loading, a well-defined scratch groove with increasing width and depth is produced (micro-ductile regime). Micro-cracks are observed for moderate normal loads (micro-cracking regime). At sufficiently high normal loads, the micro-abrasive regime is attained. However, a clear differentiation between the individual scratch regimes, in particular, the transition from micro-cracking to micro-abrasion, is challenging. For the following analysis, we therefore consider the indenter displacement monitored in situ and lateral force curves, as proposed in a previous study. The beginning of the micro-abrasive regime in the as-received soda-lime silicate glass manifests in a sudden jump in the indenter displacement and lateral force at an average scratch distance of 385 ± 6 μm, as indicated by the blue dashed line in Figure 4A. This corresponds to a mean normal load and indentation depth of 193 ± 3 mN and 1537 ± 44 nm, respectively. Chemical strengthening shifts the onset of micro-abrasion to a somewhat larger scratch distance of 399 ± 5 μm (SLS-IOX, Figure 4B). This is accompanied by a slight increase in the load threshold for abrasive wear to 199 ± 2 mN. The corresponding normal indenter displacement is somewhat lower (1524 ± 26 nm), being a direct consequence of the higher indentation hardness (see Figure S4A and Table 3). The overall changes in the abrasive wear resistance of the
commercial SLS glass induced by Na\(^+\)/K\(^+\)-ion exchange are relatively small in comparison to the effect of glass composition.\(^{63}\) Nevertheless, the presence of a surface compressive stress layer has strong consequences for micro-abrasion. The number and size of “pop-ins” in the micro-abrasive regime, indicative for chipping in front of the sliding indenter tip,\(^{27,38,110-112}\) is significantly lower in the indenter displacement and lateral force profiles of the chemically strengthened soda-lime silicate glass (SLS-IOX, Figure 4B). The corresponding optical micrographs of the residual scratch patterns are added for reference. The black pointers in the \(F_L\) curve of the as-received glass indicate the occurrence of “pop-ins” during scratching, presumably caused by individual fracture events and mostly absent from the in situ data after ion exchange (see text for details) [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 4 Examples of ramp-load scratch tests on commercial soda-lime silicate glasses (A) in the as-received state (SLS) and (B) after Na\(^+\)/K\(^+\)-ion exchange for 10 h at 450°C (SLS-IOX). Scratch tests were performed with monotonically increasing normal load up to 400 mN across a distance \(L_S\) of 800 µm (50 µm/s) using a conical indenter with a tip angle of 60° and an effective tip radius of 5.23 µm. The values of the indenter displacement \(h\) and lateral force \(F_L\) were continuously recorded during scratching (in situ, blue lines). Longitudinal profiles of the residual scratch grooves were obtained from a post-scan of the scratch track under a constant normal load of 50 µN (ex situ, red lines). The appearance of first discontinuities in the scratch profile is indicative for micro-cracking (dashed red lines). The onset of micro-abrasion manifests in a sudden jump in \(F_L\) (dashed blue lines). Shaded areas highlight the variability of these features among a set of 25 scratch tests. Optical micrographs of the residual scratch patterns are added for reference. The black pointers in the \(F_L\) curve of the as-received glass indicate the occurrence of “pop-ins” during scratching, presumably caused by individual fracture events and mostly absent from the in situ data after ion exchange (see text for details) [Color figure can be viewed at wileyonlinelibrary.com]

indenter penetration depth at the onset of micro-abrasion from 1842 ± 12 nm (AS, Figure 5A) to 1415 ± 17 nm (AS-IOX, Figure 5B). Noteworthy, the onset of micro-abrasion during scratching occurs at an indenter displacement below the maximum penetration depth of the Berkovich tip during normal indentation (see Figure 2). The observed sequence of scratch damage regimes is another indicator for our assumption that eventual concentration gradients in the tested surface layer do not have a major influence on the observed phenomena. The morphology of the resulting scratch patterns created on the surface of the chemically strengthened soda-lime silicate and aluminosilicate glasses is therefore considered as independent of gradients in chemical composition or compressive stress.

Optical inspection of a typical scratch groove (e.g., SLS, Figure 4A) reveals micro-cracking already well-below the onset of micro-abrasion. In the example of Figure 4A, the first micro-cracks occur at a scratch distance of about 164 µm. Consecutive micro-cracking is seen as the normal load increases. Radial cracks emerge alongside the scratch track and subsurface lateral cracks are also created. Chipping occurs at high load levels, when lateral cracks intersect the glass surface and start to interact with radial cracks.\(^{109}\) As will be shown in the following paragraphs, ion exchange has a very strong effect on the occurrence of these fracture events.

As a first step, we note the difference between optical inspection or post-scratch scanning and in situ observation.
Despite extensive micro-cracking, smooth parabolic indenter displacement and lateral force curves were recorded during the scratch test illustrated in Figure 5A, with no evidence of fracture (“pop-ins”) up to the onset of micro-abrasion. The formation of micro-cracks during lateral indentation, unlike the process of abrasive wear, is therefore assumed to occur predominantly during unloading, i.e., behind the sliding indenter tip. However, theoretical considerations suggest that micro-cracks may also be generated during loading. This discrepancy underlines the need for combined in situ and post-scratch monitoring of scratch-induced surface fracture. In the present case, we identify micro-cracking only from ex situ analysis of the scratch morphology (using optical imaging and post-scratch scanning, e.g., Figure 4 and Figure 5). Between in situ and ex situ analyses, the overall mismatch in penetration depth is a result of elastic recovery, in analogy to normal indentation testing. The displacement profile derived from post-scanning of the scratch groove (SLS, Figure 4A) can be divided into two segments. First, there is an initial section which exhibits a smooth displacement profile and extends to a scratch distance of around 216 µm, as indicated by the red dashed line in Figure 6A. Following this, a strongly serrated displacement profile is recorded. These discontinuities are supposed to arise from interactions of the indenter tip with the micro-cracks created during scratching. Optical inspection supports this assumption. First micro-cracks are emerging on the glass surface at a scratch distance of around 202 µm. However, a diffuse halo indicative for shallow lateral cracks is noted already at a scratch distance of about 164 µm. Here, we have to consider that the blunt conical stylus (used for scratch testing and post-scanning) can only probe surface flaws in the immediate vicinity of the scratch groove. This includes, for example, radial cracks alongside the scratch track or lateral cracks intersecting the glass surface. Lateral cracks which are confined below the glass surface as in Figure 4A are not readily visible in the post-scans. The most prominent difference between the crack patterns of the commercial soda-lime silicate glasses prior to and after Na+/K+-ion exchange (SLS, Figure 4A, and SLS-IOX, Figure 4B, respectively) is the reduced extent of lateral cracking and chipping following the ion exchange. Optical inspection of a scratch created on the surface of SLS-IOX (Figure 4B) reveals the presence of the first micro-cracks at a scratch distance of about 179 µm. This matches very well the data from the post-scan of the residual scratch groove; the longitudinal profile of the scratch track indicates the onset of micro-cracking at a scratch distance of about 185 µm.

There are some very notable differences in the distribution of the characteristic normal load levels for crack initiation between pristine and ion-exchanged glasses. A statistical evaluation of the load threshold for scratch-induced micro-cracking in the as-received and chemically strengthened glasses was conducted in order to quantify these differences.
For this purpose, the normal load at the onset of micro-cracking was examined for a series of up to 25 ramp-load scratch tests per glass, utilizing the information derived from the post-scans of the residual scratch grooves. The results of this analysis are depicted in Figure 6A for SLS and AS before and after IOX (due to the qualitative similarity between both glasses, we will focus our discussion on the SLS glass). For the as-received SLS glass, normal loads ranging from 19 mN to 114 mN were required to generate the first micro-cracks at the glass surface, even though all scratch tests were performed under identical experimental conditions. The cumulative probability \( F(P) \) indicates a well-separated bimodal distribution of the characteristic normal load values. The corresponding probability density \( f(P) \) plot supports this observation, showing two maxima centered at around 41 mN and 109 mN (peak fitting was carried out on the assumption of a normal distribution of the normal load values; normal load values corresponding to the probability density maxima of the two fracture modes are summarized in Table S1). Complementary optical analysis of the residual scratch patterns confirmed the presence of two different failure mechanisms. The first failure mode, which gives rise to the maximum centered at a relatively low normal load of around 41 mN (SLS, Figure 6A), is attributed to occasional failure originating from interactions of the indenter tip with pre-existing surface flaws. In such cases, the creation of micro-cracks is readily visible in the \textit{in situ} recorded lateral force profiles in form of sudden discontinuities or “pop-ins” (see Figure S5). The failure mode responsible for the occurrence of the second maximum centered at higher normal load is assigned to scratch-induced micro-cracking in the absence of a critical surface flaw. Evidence for the activation of this failure mode is only available from an \textit{ex situ} analysis of the permanent scratch groove formed on the glass surface (as previously discussed by way of example in Figure 4A for the as-received SLS glass), indicating that this failure mode occurs upon unloading. The latter failure mode (starting at moderate normal loads from about 101 to 114 mN in the case of SLS, Figure 6A) is therefore assumed to represent the materials resistance to scratch-induced micro-cracking, in contrast to the occasional mechanical failure observed at normal loads in the range of about 19 mN to 52 mN, which is assigned to specimen surface quality. Following IOX, the cumulative probability plot of microcracking events changes from bimodal to a monomodal distribution (Figure 6A, in the case of SLS with the exception of two outliers). The maximum probability density for this single mode is at \( \sim 91 \) mN for SLS-IOX and at \( \sim 105 \) mN for AS-IOX, consistently down-shifted from the upper micro-cracking mode seen on the untreated glasses. The low-load micro-cracking mode is completely suppressed in the two glasses after IOX, indicating that the surface compressive stress counteracts occasional fracture events related to surface flaws. It will be interesting to explore how dedicated adjustments of the surface stress profile may provide additional advantages in this regard.\(^\text{116}\)

On average, a normal load of \( 126 \pm 5 \) mN and \( 109 \pm 5 \) mN is necessary during scratching (using the employed tip geometry, high-load micro-cracking regime) to induce micro-cracking in the untreated AS and SLS glasses, respectively. The load threshold for micro-abrasion depicted in Figure 6B follows the same trend (as already discussed with reference to Figure 4A and Figure 5A; normal load values corresponding to the probability density maxima are summarized in Table
S1), demonstrating the enhanced defect resistance of untreated aluminosilicate glasses over conventional SLS.\textsuperscript{65,84-88} Interestingly, ion exchange reduces this load threshold to $105 \pm 13$ mN (AS-IOX) and $91 \pm 2$ mN (SLS-IOX), respectively. This points to a reduced resistance to scratch-induced surface damage following IOX, and is—on first view—counterintuitive. For a better understanding of this effect (which is not accessible through normal indentation experiments such as shown in Figure 3),\textsuperscript{15-19,21} the experimental values of lateral force were converted into a representative lateral indentation stress $\sigma_r$.

$$\sigma_r = \frac{F_L}{A_{\tan}}.\quad (15)$$

Assuming spherical contact behavior at the apex of the conical stylus, and neglecting the effects of sink-in or pile-up, the projected tangential area in the scratching direction is estimated by\textsuperscript{27}

$$A_{\tan} = R_{\text{tip}}^2 \arccos \left( 1 - \frac{h}{R_{\text{tip}}} \right) - \left( R_{\text{tip}} - h \right) \sqrt{2R_{\text{tip}}h - h^2},\quad (16)$$

where $R_{\text{tip}} = 5.23$ µm. The idealized $\sigma_r$ therefore depends on normal load $P$, as illustrated in Figure 7. Although Equation (16) is a strong simplification,\textsuperscript{25} it still provides a valuable estimate of the critical stress levels at which scratch-damage is induced. For all glasses, a monotonic increase of $\sigma_r$ with increasing normal load is seen at the beginning of the scratch test (under ramp-loading). In SLS, occasional cracking (visible in bursts in the calculated $\sigma_r$, red curves in Figure 7) occurs at about $3.46 \pm 0.13$ GPa, probably indicative for the type and size of preexisting surface defects. The higher-load micro-cracking regime starts at a stress of about $4.49 \pm 0.23$ GPa. Directly before the onset of micro-abrasion, a stress plateau is reached where the magnitude of $\sigma_r$ stays almost constant at $\approx 5.21 \pm 0.08$ GPa, even though the normal load is further increased. The abrupt increase in the lateral indentation stress at a normal load of $193 \pm 3$ mN is associated with the transition from micro-cracking to micro-abrasion and sets the upper boundary for this segment. Closer examination of the plateau region reveals the presence of small discontinuities (or serrations) in the lateral indentation stress profiles, indicative for abrasive wear or stick-slip reactions at the glass surface. Optical inspection of the residual scratch patterns corroborates this finding (first visible signs for micro-abrasion can be detected within the respective range of normal loads). However, the exact physical meaning of this phenomenon is unclear for the moment. With regard to the incipient micro-abrasion and the sudden jump in the lateral indentation stress at the end of the plateau region, we may speculate that a transitory regime is entered during which the prevailing mechanism of material removal at the glass surface is changing from micro-cracking to micro-abrasion. Owing to the dynamic character of lateral indentation,\textsuperscript{117} a certain scratch distance may be required for this procedure, as indicated by the dashed arrows in Figure 7. It remains to be explored how modifications in the loading

![Figure 7](https://example.com/figure7.png)

**Figure 7** Normal load dependence of the representative lateral indentation stress $\sigma_r$ for commercial soda-lime silicate (SLS) and aluminosilicate glasses (AS): (A) SLS before and after Na+/K+-ion exchange for 10 h at 450°C (SLS-IOX). (B) AS glass before and after Na+/K+-ion exchange for 6 h at 420°C (AS-IOX). Values of $\sigma_r$ were determined from the ratio between the lateral force and the projected tangential area assuming a simplified spherical contact. Shaded areas highlight the variability in the normal load $P$ and of $\sigma_r$ associated with the onset of micro-cracking and micro-abrasion, respectively (each curve represents an individual scratch experiment; scratch tests with occasional micro-cracking at relatively low normal loads are highlighted in red) [Color figure can be viewed at wileyonlinelibrary.com]
ramp or scratching speed would affect this observation. The normal load at which the plateau evolves, the plateau’s lateral extent and the magnitude of the corresponding lateral σ, seem to strongly vary with the glass composition and the employed post-processing conditions (i.e., pristine vs. ion exchanged).

Considering the normal load dependence of the resistance against micro-cracking, it is somewhat unexpected that the earlier mentioned differences in the crack resistance between the commercial soda-lime silicate and aluminosilicate glasses do not also reflect in a variation of the lateral indentation stress. Instead, equivalent values of σ, are estimated for the pristine soda-lime silicate (4.49 ± 0.23 GPa for SLS) and aluminosilicate glasses (4.54 ± 0.14 GPa for AS). We may explain this result by the differences in the normal load dependence of the lateral indentation stress between these two glass types. The lower scratch hardness of the as-received aluminosilicate glass (7.1 GPa for AS, as compared to 7.5 GPa for SLS, see Table 3) leads to a slower build-up of the lateral indentation stress during loading, thereby shifting the onset of micro-cracking to higher normal loads in comparison to the soda-lime silicate glass. The same argumentation seems to hold at least partially for the reduced load threshold for micro-cracking in the chemically strengthened soda-lime silicate and aluminosilicate glasses. Following the Na\(^+\)/K\(^+\)-ion exchange, a surface compressive layer with enhanced indentation hardness and scratch resistance is created (see Table 3). Accompanied by the enhanced scratch hardness, also higher levels of lateral indentation stress are build-up in a ramp-load scratching experiment on the chemically strengthened glasses (SLS-IOX, Figure 7A and AS-IOX, Figure 7B). In combination with the lower level of lateral indentation stress associated with the onset of micro-cracking in these glasses (4.19 ± 0.09 GPa for SLS-IOX and 4.10 ± 0.25 GPa for AS-IOX), a reduction in the crack resistance is induced by the Na\(^+\)/K\(^+\)-ion exchange. The latter is probably a result of the increased packing density in the surface compressive layer, which is relatively more pronounced in the AS glasses. For example, for normal indentation experiments, it is well established that compacted silicate glasses (e.g., through hot-compression\(^{120}\)) are more susceptible to micro-cracking in comparison to their pristine counterparts.\(^{46,86,121}\) In ion-exchanged glasses, this detrimental effect is normally balanced by the parallel creation of residual surface compressive stress, which effectively suppresses the initiation of micro-cracks during normal indentation (see Figure 3).\(^{15-19,21}\) However, in the more sensitive experiment of blunt scratching, the reduced crack resistance is very well resolved. Finite element modeling of the stress field during lateral loading\(^{108,112,113}\) may provide further insight on this effect.

4 CONCLUSIONS

In summary, we have investigated the elasticity, plastic deformation and surface fracture of chemically strengthened soda-lime silicate and sodium aluminosilicate glasses during normal indentation and scratch testing. Chemically strengthened soda-lime silicate and aluminosilicate glasses were produced through a Na\(^+\)/K\(^+\)-ion exchange, creating a surface compressive layer in the range of 600 MPa (SLS-IOX) to 900 MPa (AS-IOX). To differentiate the effects of the compressive layer from variations in chemical composition caused by ion exchange, bulk glasses with variable Na\(_2\)O-to-K\(_2\)O molar ratio were produced and studied for reference. Instrumented indentation using a conventional indenter set-up corroborated previous findings on the effects of chemical strengthening on surface Young's modulus, hardness and indentation cracking. Using lateral indentation in the elastic-plastic regime, we found a marked increase in the scratch hardness as a result of chemical strengthening, which manifest in higher work of deformation required for creating the scratch groove. In this, the glass composition seems to play a stronger role than the absolute magnitude of surface compressive stress. Switching from a sharp Berkovich indenter in edge-forward orientation to a blunt conical stylus provides access to the more intricate features of the scratch response, in particular, the onset of micro-cracking and abrasive wear. Scratch-induced micro-cracking at low loads is attributed to occasional mechanical failure caused by perturbation or flaws alongside the scratch path. The creation of a surface compressive layer drastically reduces the susceptibility to such defects. This highly beneficial effect is, however, accompanied by a parallel reduction of the load threshold for micro-cracking in the ion-exchanged glasses. Finally, the onset stress of micro-abrasion is enhanced by the presence of a surface compressive stress field, and extensive chipping such as usually observed during abrasive damage on glass surfaces is largely suppressed.

ACKNOWLEDGEMENTS

This project received funding from the German Federal Ministry of Education and Research (project 3TGlass; grant no. 01DL166006A). The authors thank all members of the project consortium for fruitful discussion and technical support. Furthermore, the authors with to thank their colleagues Roman Sajzew and Christian Zeidler for conducting confocal microscopic analysis.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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SUPPORTING INFORMATION
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How to cite this article: Sani G, Limbach R, Dellith J, Sökmen İ, Wondraczek L. Surface damage resistance and yielding of chemically strengthened silicate glasses: From normal indentation to scratch loading. J Am Ceram Soc. 2021;104:3167–3186. https://doi.org/10.1111/jace.17758