**Elastic-plastic deformation in ion-exchanged aluminosilicate glass by loading
rate dependent nanoindentation**

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Abstract:

The elastic-plastic deformation in raw and ion-exchanged aluminosilicate glass is investigated by loading rate dependent nanoindentation. The nanohardness and Young's modulus of the raw and ion-exchanged glasses at different loading rate (100-20,000 $\mu\text{N}\cdot\text{s}^{-1}$) are explored up to a maximum load of 9,000 μN . The nanoindentations are scanned with AFM to observe the morphology of the indents. The results show that Young's modulus of the aluminosilicate glass increases after ion exchange and that the nanohardness of the raw and ion-exchanged aluminosilicate glass increases linearly with the loading rate, when plotted on a double logarithmic

axes. However, the nanohardness of the raw glass is more sensitive to the variation of loading rate. The compressive stress on the ion-exchanged glass can inhibit plastic deformation. These results are explained in terms of shear stress underneath the indenter and the number of the flow lines in the nanoindentations. These findings are useful for better understanding the dynamic contact-induced damage growth mechanisms of ion-exchanged glass.

Key words: Elastic-plastic deformation; Nanoindentation; Loading rate; Ion exchanged glass

1. Introduction

Ion exchange, also known as chemical strengthening, is a process whereby the original glasses are immersed into a molten alkali salt at a temperature below the glass transition and this results in glass strengthening [1-4]. Ion-exchange has been used for one century to modify the surface properties of glass [5]. As the main material for fabricating touch panels of popular display devices, as well as forward facing aircraft and other windscreens, the scratch-proof property is an important requirement [3, 6]. The hardness, which is apparently related to abrasion resistance, has often been used as an approximate measure of the scratch-proof resistance property [7]. Indentation is a convenient method to evaluate mechanical properties such as hardness and Young's modulus [8]. The indentation process involves the elastic-plastic deformation of materials [9, 10]. According to Johnson [11, 12], the indentation process can be divided into three distinct regimes, including elastic, elastic-plastic and fully plastic. The elastic-plastic transition regime is hard to understood due to its complexity of the

combination of elastic and plastic deformation process. The indentation method can be applied to research the elastic-plastic transition phenomenon. For example, Wright et al. [13] indicated that the onset of plasticity during nanoindentation of a Zr-based bulk metallic glasses (BMGs) occurred at a discrete displacement burst (named as “pop-in”). The elastic-plastic transition on single crystals of platinum was studied statistically with nanoindentation as a function of temperature and indentation rate by Mason et al. [14]. The “pop-in” phenomenon which is related to the elastic-plastic transition regime in indentation experiments is also observed in ceramic and glass materials. The onset of plasticity was seen as a sudden displacement discontinuity in the load-displacement curves in low-load indentation experiments in ceramic single crystals by Page et al. [15]. Mao et al. [16] indicated that the first “pop-in” indentation loads for the C plane of sapphire single crystal gradually decreases as loading rates increase. Dey et al. [17] observed “pop-in” phenomenon in load-displacement plots in soda-lime-silica glass, and related those displacement bursts with the formation of deformation bands inside the nanoindentation cavity.

During the indentation tests, the rate of loading is an important parameter especially for brittle materials as it strongly affects the damage evolution [18]. Clear understanding of the effect of loading rate on the elastic-plastic deformation of the glass will provide valuable insight into the damage growth mechanisms especially during dynamic contact events of brittle solids [19, 20]. Rate dependence in the response of the near-surface region probed by indentation on glasses and ceramics has been intensively studied [17, 19, 21-31] in different ranges of applied load with some

interesting results being obtained. For nanoindentation, the nanohardness of glasses and ceramics is reported to remain unchanged [32], slightly reduced [33] or increased with loading rate [19, 22]. Schuh et al. [34] indicated that the indentation load-displacement curve in their study on a Pd-40Ni-20P BMG is strongly dependent on the indentation strain rate. For the ion-exchanged glass, the surface compressive stress can inhibit crack propagation, and lead to increased strength [35, 36] and hardness [18, 37]. However, the influence of loading rate on the nanohardness of ion-exchanged glasses still remains unknown.

The main object of this study is to investigate the effect of the loading rate variation ($100\text{-}20,000\mu\text{N.s}^{-1}$) on the nanohardness of the raw and ion-exchanged glasses with different surface compressive stress. In this study, it is shown that the nanohardness of the raw aluminosilicate glass increases linearly with loading rate in double logarithmic axes. The effect of loading rate on the nanohardness of the ion-exchanged glass is similar to that on the raw glass. However, the nanohardness of the raw glass is more sensitive to the variation of the loading rate. These results are explained in terms of shear stress underneath the indenter and the flow line phenomena in the nanoindentations.

2. Experiments

The glass used was a float glass of thickness, 4 mm, with the same composition as in our previous published research [36-38]. Ion exchange involved suspending the aluminosilicate glasses in a molten potassium nitrate bath held at 420 °C for different

times (1, 12 and 48 hours). Then the glass samples were removed, cooled, and rinsed with deionized water after ion exchange.

The compressive Stress (CS) and depth of stress layer (DOL) of glass samples were measured by the surface stress meter (FSM-6000LE, ORIHARA, Japan) which is based on the theory of photoelasticity [39]. The glass sample was placed in the measuring area and care is taken to make sure the glass surface fits with the triple prism to ensure the birefringence fringes were detectable and clear. Parameters such as thickness, refractive index, photoelastic constant of the glass are input into the analysis [40]. Then, the CS and DOL values are obtained. The systematic error for the CS and DOL was ± 20 MPa and ± 2 μm , respectively. Each glass sample was measured at five random positions and the average CS and DOL values were obtained.

A nanoindenter (TI 950 Triboindenter, Hysitron) with a full-scale capacity of 10 mN was used for all indentation experiments. A Berkovich diamond indenter was used for measuring the nanohardness and Young's modulus. Calibration was performed using a standard fused silica sample prior to the nanoindentation of the glass samples. The method used in the experiments and calculations was based on ISO 14577 [41]. The nanohardness and Young's modulus data were calculated using the well-known method developed by Oliver and Pharr (referring to it as OP method) [42]. In the present experiments, the load was increased up to 9,000 μN . This is with loading rate changed in the range of 100-20,000 $\mu\text{N.s}^{-1}$. At least six indentation experiments were performed at each given loading rate. After indentation testing, all

the impressions were imaged using a scanning probe microscopy (SPM) provided by the indentation system to confirm the reproducibility of the nanoindentations. The nanoindentations were further scanned with an atomic force microscope (AFM) (Dimension Edge, Bruker, Germany) to observe the morphology of the impressions.

3. Results

The compressive stress (CS) and depth of stress layer (DOL) values of the ion-exchanged specimens for different exchange time are shown in Table 1. It can be seen that the CS decreases and the DOL increases with the ion-exchange time continuously.

Table 1 Compressive stress (CS) and depth of stress layer (DOL) results for aluminosilicate glasses with different ion-exchange time

Ion-exchange time (h)	1	12	48
CS (MPa)	747 ± 20	710 ± 20	640 ± 20
DOL (μm)	15 ± 2	43 ± 2	77 ± 2

The typical load-depth curves for the raw and the ion-exchanged glass (with 1 hour immersion time) are shown in Fig. 1 (a) and (b), respectively. The inserted picture (top left) shows the corresponding in situ SPM images of the six nanoindentations. It can be seen that the shapes and sizes of the nanoindentations are similar and all six load-depth curves are very similar and lie on top of each other.

The recovery ratios which are defined as the ratio between the final depths of penetration (h_f) and the maximum depths of penetration (h_{max}) of the raw and

ion-exchanged glasses for different times are shown in Fig. 2. The recovery ratio decreases with increasing the loading rate for both the raw and ion-exchanged specimens, implying that the elastic depth recovery increases. The results also show that the recovery ratio of the raw glass is higher than that of the ion-exchanged specimens and this parameter decreases when the ion-exchange time is prolonged.

Fig. 3 shows typical load-depth (P - h) plots for the raw and the ion-exchanged glass with 1 hour immersion time at different loading rates in the range of 100-20,000 $\mu\text{N.s}^{-1}$. The magnified view of the loading parts for the raw glass and the ion-exchanged glass with 1 hour immersion time are shown in Fig. 3 (b) and 3 (d), respectively. The indentation curves are clearly affected by the loading rate. With the increase of loading rate, the depth at the end of loading (h_{max}) is decreased. It can be seen that the P - h curves are punctuated by many discrete bursts of rapid displacement, at nearly constant load, which are called serrations. The serrations are more pronounced at lower loading rates than at higher loading rates which is in consistent with previous work [19].

The nanohardness and Young's modulus results of the raw and the ion-exchanged glasses as a function of loading rate are shown in Fig. 4 (a) and (b), respectively. The nanohardness of the raw glass increases by ~10.9% with increase in loading rate from 100 to 20,000 $\mu\text{N.s}^{-1}$. For the ion-exchanged glasses, the nanohardness increases in the same range of loading range by ~6.6%, ~8.1%, and ~8.5%, for ion-exchange immersion times of 1, 12, and 48 hours respectively. The Young's modulus of the raw glass approximately increases by ~2.3% at the same range of loading rate. However,

the variation of the Young's modulus of the ion-exchanged glasses with loading rate is very small (increases less than 1.0%).

The sensitivity to loading rate, m , is defined as the slope of the plot of indentation hardness (H) as a function of loading rate (ν) in double logarithmic axes [43]. As shown in Fig. 5, the nanohardness increases linearly with loading rate when plotted with double logarithmic axes. The values of m of ion-exchanged glasses are lower than that of the raw glass.

The projected area of the nanoindentation site of the raw and ion-exchanged glasses as a function of loading rate is shown in Fig. 6. The projected area of the raw glass decreases by 10.6% while the same parameter of the ion-exchanged glasses with 1, 12, and 48 hour immersion times decreases by 7.3%, 7.8%, 8.9%, respectively.

Typical AFM images of nanoindentations on the raw glass for a maximum load of 9,000 μN at different loading rates are shown in Fig. 7. Similar, AFM images of nanoindentations on the ion-exchanged glass with 1 hour immersion time are shown in Fig. 8. It can be seen that a large number of flow lines (see arrows) are present inside the nanoindentations. The flow lines are more pronounced in the nanoindentations produced at lower loading rates. The ridges and troughs in the nanoindentations in Fig. 7 show that the flow lines in the raw glass are more noticeable than those of the ion-exchanged glass in Fig. 8. Fig.9 shows typical cross-section profiles in nanoindentation on the raw glass (Fig. 9c) and on the ion-exchanged glass with 1 hour immersion time (Fig. 9d) at loading rate of 100 $\mu\text{N.s}^{-1}$. It can be seen that there shows abrupt height changes in shear planes. The

height of the shear planes in nanoindents on the raw glass (Fig. 9c) is larger than that on the ion-exchanged glass (Fig. 9d).

4. Discussion

The reproducibility of the six load-depth curves in Fig. 1 confirms the accuracy of the results obtained from the nanoindentation experiments. The recovery ratios (Fig. 2) of the raw and ion-exchanged glasses for different exchange times are well within the ratio of 0.7, which is suggested threshold below which the Oliver and Pharr method [42, 44] is applicable. The recovery ratio of the raw glass is higher than that of the ion-exchanged specimens, indicating that the elasticity of the ion-exchanged specimen is greater than that of the raw glass (i.e. the higher the recovery ratio (h_f/h_{max}), the lower the elasticity). Tandia [45] found that the strain induced by ion-exchange is entirely elastic, that is to say, when a reverse ion exchange is performed to swap the original ions back into the glass, the initial volume of the as-melted glasses is entirely recovered. Also, to be noted, the Young's modulus of ion-exchanged glasses (shown in Fig. 4) increases by about 2 % after ion exchange. The nanohardness values of ion-exchanged glasses are greater than that of the raw glass, and this is caused by the CS on the surface of ion-exchanged glasses [37]. The influence of DOL on hardness is little when indentation depth is much smaller than DOL. From Table 1, it can be seen that the values of DOL (greater than 15 μ m) are much larger than the nanoindentation depth (about 250 nm, shown in Fig. 1). Thus the influence of DOL on nanohardness is little.

The irreversible deformation in indentation tests has been regarded as plastic deformation [46], which is divided into two components: densification and shear flow [47-49]. The deformation of glasses is dependent on both glass structure and contact geometry. Blunter contacts promote greater densification. The deformation mechanism changes to shear flow when contacts becomes sharper [50]. For the normal glass (glasses with a substantial component of network modifiers [51]), it deforms to a large extent by shear flow mechanism. Whilst for the anomalous glass (silica-rich glasses [51]), it deforms primarily by densification [50]. It is reported that the plastic deformation volume is greater than the densified volume when the silica content is less than about 70% [52]. Thus, the aluminosilicate glass used here with a silica content of 63.5%, mainly deforms by shear flow mechanism with a relatively sharp Berkovich indenter.

It is noted that aluminosilicate glass is a homogeneous, isotropic, non-crystalline solid, however, it is suggested that shear flow occurs by an inhomogeneous mechanism e.g. large shear displacements occur on certain planes at an atomistic length scale [22, 48]. These preferred shear planes occur at positions of structural weakness where they may be links to non-bridging oxygen and weaker ionic bonds composed of network modifiers e.g. Na^+ , K^+ ions [17, 19]. The pronounced serrations in Fig. 3 are believed to link to the bursts of those instantaneous shear flow processes, with the first burst of the serrations directly related to the initiation of plastic deformation of glass [19, 53]. The proposal is that the critical load where the first serration burst is a good measure of the intrinsic flow properties of the glass. The

218 serration phenomenon in Fig. 3 is similar to that found in the load-depth plots of bulk
 219 metallic glasses [34, 53-56] and is first recognized by Mukhopadhyay et al. [17, 19,
 220 22, 24] in soda-lime glass. To find the critical load, which represents the onset of
 221 plastic flow, the focus will be on the initial stages of nanoindentation (i.e. the initial 4
 222 nm indentation depth in load-depth as shown in Fig. 10) for the raw glass and the
 223 ion-exchanged glass with 1 hour immersion time. The solid lines in Fig. 10 are the
 224 predicted results based on Hertzian contact theory which represent a completely
 225 elastic response. Rapid depth excursions are observed in the loading curves as
 226 denoted by the black filled points in Fig. 10a and Fig.10b. These “pop-ins”
 227 correspond to the spikes in the velocity response shown in Fig. 10c and Fig. 10d.
 228 Indentations beyond the first “pop-in” exhibit measurable residual displacements after
 229 unloading [53]. It is found that these critical loads are rate dependent and is 4.6, 40.6,
 230 48.5 and 157.6 μN for the raw glass at loading rate of 100, 1000, 2000, and 10,000
 231 $\mu\text{N.s}^{-1}$, respectively. The critical loads are 9.9, 55.6, 67.1 and 260.3 μN for the
 232 ion-exchanged glass with 1 hour immersion time at loading rate of 100, 1000, 2000,
 233 and 10,000 $\mu\text{N.s}^{-1}$ respectively. Similarly, the critical loads for the ion-exchanged
 234 glasses with 12 and 48 hours immersion time can be obtained. It is worth noting that
 235 when the loading rate is high enough, the serrations are not as prominent as those
 236 obtained at lower loading rates. Thus, it is very difficult to identify the first
 237 displacement burst at loading rate 20,000 $\mu\text{N.s}^{-1}$. This is in consistent with the
 238 previous work [17] and it is attributed to the suppression of shear slippage when
 239 loading rate is high. In addition, the noise of the instrument becomes large when the

loading rate is really high, and this may also cause the difficulty to find the critical load at a loading rate of 20,000 $\mu\text{N.s}^{-1}$. However, since the shear stress is suppressed when loading rate increases, the onset of plastic flow is set back. Therefore, it is reasonable to assume that the critical load at loading rate 20,000 $\mu\text{N.s}^{-1}$ is higher than that at a lower loading rate [17, 22]. In addition, previous indentation results show that there is little influence of friction on the contact analysis [44, 57, 58]. Thus, the variation of friction coefficient between the indenter tip and the glass at different loading rate is not considered in this analysis.

The contact between the Berkovich indenter and the thin glass surface can approximately be described by the Hertzian elastic prediction [19], and the shear stress (τ) correspond to the critical load can be calculated as [19, 59],

$$\tau = 0.445 \left(\frac{16P_{critical}E_r^2}{9\pi^3R_{tip}^2} \right)^{1/3} \quad (1)$$

where $P_{critical}$ represents the critical load got from the load-depth curves. R_{tip} is the radius of the indenter with a value of 150 nm for the Berkovich indenter used here.

E_r is the reduced modulus which is given by [42]

$$\frac{1}{E_r} = \frac{1-\nu_{glass}^2}{E_{glass}} + \frac{1-\nu_{indenter}^2}{E_{indenter}} \quad (2)$$

where E is the Young's modulus, ν is Poisson's ratio for the glass and the indenter tip. For a diamond Berkovich indenter, the $E_{indenter}=1140$ GPa, $\nu_{indenter}=0.07$ [53].

Substituting the Young's modulus and critical load values into Eqs. (1) and (2), the critical shear stress values can be obtained. The critical shear stress of the raw and ion-exchanged glasses as a function of loading rate is shown in Fig. 11. The critical

shear stress increases with loading rate for both the raw and the ion-exchanged glass. The variation trend of critical shear stress with loading rate is similar to the tendency of nanohardness with loading rate, Fig. 4a. It can also be seen that the critical shear stresses of the ion-exchanged glasses are larger than that of the raw glass at the same loading rate, and this may be attributed to the compressive stress on the surface of the ion-exchanged glasses can inhibit the onset of the plastic flow [18].

To find the relationship between nanohardness and critical shear stress, the correlation of these two parameters is shown in Fig. 12. The nanohardness increases almost linearly with critical shear stress for both the raw and ion-exchanged glasses, indicating that the variation of the critical shear stress is the main reason for the variation of the nanohardness at different loading rate, and this result agrees with previous works [19, 60]. In addition, the slope of the nanohardness of the raw glass as a function of the critical shear stress is higher than that of the ion-exchanged glasses, implying that the nanohardness of the raw glass is more sensitive to the variation of loading rate than the ion-exchanged glasses. Hardness is defined as the ability of materials to resist plastic deformation. The compressive stress on the surface of ion-exchanged glasses can inhibit plastic deformation and damage evolution, especially at higher loading rate [18], and this may lead to the lower sensitivity of the nanohardness of the ion-exchanged glass to loading rate.

The serrations in Fig. 3 are closely related to the formation of the flow lines in the nanoindentations shown in Fig. 7 and 8. The flow lines phenomenon is in accordance with the previous work [61] in which the flow lines are regarded as shear faults of

negligible thickness produced by shear displacements. It is reported that each serration in the load-displacement curve corresponds to the nucleation of individual shear fault in metallic glasses [54]. The contact of a sharp-pointed indenter on glass surface produces a highly concentrated stress field. With the development of any shear fault, some stress relaxation process must accompany [62], and this may lead to the “pop-ins” (rapid depth excursions, relatively load drop) shown in Fig. 10. The load at which these flow lines first occur is a measure of the basic plastic properties of the glass [61]. The plastic strains appear to be concentrated on the shear faults, and there is only elastic strain between them [63]. Hagan [61] pointed out that the flow lines would intersect with each other and generate kinking. It is difficult to continue to slide once the kinking is generated. Thus, a new flow line in the neighborhood of the kinked flow line will be activated. This may lead to a larger contact area and results in a lower nanohardness. The number of flow lines produced at higher loading rate is less than that at lower loading rate, agreeing with previous work [19]. Thus, there are fewer intersection and kinking at higher loading rate. As a result, the contact area of the nanoindentation produced at higher loading rate is smaller than that at lower loading rate (in line with the results shown in Fig. 6). This may lead to the increase of nanohardness with loading rate. The compressive stress on the surface of the ion-exchanged glass can suppress the plastic deformation of the glass [18]. Thus, the flow lines in the nanoindentations on the ion-exchanged glasses are less remarkable than that on the raw glass (Fig. 9), leading to higher nanohardness values but lower nanohardness rate sensitivity of the ion-exchanged glass.

5. Conclusions

The Young's modulus of the raw aluminosilicate glass increases by ~2.3% after ion exchange. However, the variation of the Young's modulus of the ion-exchanged glasses with loading rate is very small (increases less than 1.0%).

The nanohardness of the raw aluminosilicate glass increases by ~10.9% with increase in loading rate from 100 to 20,000 $\mu\text{N}\cdot\text{s}^{-1}$. Meanwhile, the nanohardness of the ion-exchanged glasses, with 1, 12, and 48 hour immersion times, increases by ~6.6%, 8.1%, and 8.5% respectively, for the same range of loading rate.

The nanohardness of the raw and ion-exchanged aluminosilicate glass also increases linearly with the loading rate in double logarithmic axes, and this is attributed to the increase of critical shear stress with loading rate. However, the nanohardness of the raw glass is more sensitive to the variation of loading rate. The critical shear stresses of the ion-exchanged glasses are larger than that of the raw glass at the same loading rate, and this may be attributed to the compressive stress on the surface of the ion-exchanged glasses can inhibit the onset of the plastic flow. The serrations in the load-depth curves are closely related to the formation of the flow lines in the nanoindentations. The number of flow lines in the nanoindentations produced at comparatively higher loading rate is less than that at lower loading rate, and this may lead to a smaller contact area and results in a higher nanohardness at higher loading rate. This may be another reason that leading to the increase of nanohardness with loading rate. The number of the flow lines in the nanoindentations

on ion-exchanged glasses is less than those in the raw glass, leading to a larger nanohardness of ion-exchanged glasses.

Latest generation forward facing windscreens on commercial aircraft, as well as touch panels of popular display devices, now use chemically toughened glasses and the results in this paper are thought to be of much value for better understanding the dynamic contact-induced damage growth mechanisms of ion-exchanged glass.

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Figure captions

Fig1.TIF Typical load-depth curves for: (a) loading and unloading of the raw glass; (b) ion-exchanged specimen, with 1 hour immersion time. For both cases, the top left inserted picture shows the corresponding SPM images of the six nanoindentations.

Fig2.TIF Recovery ratio (h_f/h_{max}) of raw and ion-exchanged glass, with 1, 12 and 48 hour immersion time, as a function of the loading rate.

Fig3.TIF Typical load-depth plots for raw and ion exchanged glass: (a) raw; (b) magnified view of the loading parts for raw; (c) ion-exchanged glass with 1 hour immersion time; (d) magnified view of the loading parts for ion-exchanged glass with 1 hour immersion time.

Fig4.TIF Effect of loading rate on raw and ion-exchanged glasses: (a) Nanohardness; (b) Young's modulus.

Fig5.TIF Logarithmic plot of indentation hardness (H / GPa) versus loading rate ($v / \mu\text{N.s}^{-1}$).

Fig6.TIF Projected area of raw and ion-exchanged glasses as a function of loading rate.

Fig7.TIF Typical AFM images of nanoindentations on raw glass with a maximum load of 9000 μN at loading rates of: (a) 100; (b) 1000; (c) 2000 and (d) 20,000 $\mu\text{N.s}^{-1}$. Arrows are highlighting some of the flow lines.

Fig8.TIF Typical AFM images of nanoindentations on ion-exchanged glass with 1 hour immersion time with a maximum of load of 9000 μN at loading rates of: (a) 100; (b) 1000; (c) 2000 and (d) 20,000 $\mu\text{N.s}^{-1}$. Arrows are highlighting some of the flow

lines.

Fig9.TIF Typical AFM image of nanoindentation on raw glass (a) and on ion-exchanged glass with 1 hour immersion time (b) at loading rate of $100 \mu\text{N.s}^{-1}$; (c) Three typical cross-section profiles along the green arrows in (a); (d) Three typical cross-section profiles along the green arrows in (b).

Fig10.TIF Typical load-depth response at loading rate $100 \mu\text{N.s}^{-1}$ of: (a) raw glass; (b) ion-exchanged glass with 1 hour immersion time demonstrating departure from the elastic portion at the plastic yield point. It is to be noted that sudden depth excursions in (a) and (b) correspond to spikes in the velocity response shown in (c) and (d), respectively. The solid (red) lines on (a) and (b) are the fitting results with the Hertzian equation.

Fig11.TIF Critical shear stress of raw and ion-exchanged glasses as a function of loading rate.

Fig12.TIF Nanohardness of raw and ion-exchanged glasses as a function of critical shear stress. The solid lines are the linear fitting results.

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Fig 1

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Fig 7

Fig 8

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Fig 12

Table 1 Compressive stress (CS) and depth of stress layer (DOL) results for aluminosilicate glasses with different ion-exchange time

Ion-exchange time (h)	1	12	48
CS (MPa)	747 ± 20	710 ± 20	640 ± 20
DOL (μm)	15 ± 2	43 ± 2	77 ± 2