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Fracture strength of ion-exchange silicate-containing dental glass ceramics

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Abstract Dental glass ceramics with the composition of $(0.2K, 0.8Na)_2O–xAl_2O_3–ySiO_2$ (x = 0.4–0.8, y = 4–6) were studied for their mechanical properties. Different ion-exchange practices were used to modify the sub-surface concentration distributions of K^+, Na^+, and H^+ of these glass ceramics. Specimens were heat-treated in molten KNO_3, and $NaNO_3 + KNO_3$ salt baths at 350–450 °C for the ion exchanges of K^+ and Na^+, or in the 4% acetic aqueous solution at 85 °C for a hydration treatment. Some glass ceramics contained a feldspar crystalline phase, which was not affected by different ion-exchange practices. Specimens with a single ion-exchange process or with the hydration treatment had higher flexural strength than those without either of these two treatments. For double ion-exchange specimens, the flexural strength increased with decreasing ion-exchange temperature. The double ion-exchange specimens had flexural strength up to 280 MPa, which was slightly lower than that of the single ion-exchange specimens, but much higher than that of the as-annealed specimens. However, the Weibull modulus of these double ion-exchange specimens was 5–8 because of the presence of large defects. For further increasing mechanical reliability, silicate-containing dental glass ceramics were required to have appropriate flaw controls and ion-exchange processes.

Introduction

With the behaviors of low toughness and high flaw-sensitivity, most glasses are limited in mechanical applications for dental materials [1–4]. Introduction of a second phase in the glass matrix has been used to improve fracture strength [5, 6]; however, mechanical reliability of these dental glass ceramics is still low. Recently, Green et al found some glasses become flaw-insensitive or highly reliable after a surface-modification technique to properly design the profile of residual stresses in the glass subsurface [7–10]. This finding suggests us to re-evaluate the mechanical reliability of dental glasses, especially those silicate glasses containing both K^+ and Na^+ cations. One of the flaw-insensitive glasses previously studied is from the $SiO_2–Al_2O_3–Na_2O–K_2O$ system, and this commercial glass has a similar composition as some dental glass ceramics [2–6, 11–14]. Therefore, silicate-containing dental glass ceramics might have high mechanical reliability if they are appropriately prepared.

Surface coating, glazing, thermal tempering, and ion exchange methods have been used to control the distributions of residual stresses on the glass surfaces. For silicate-containing glasses, the ion exchange of K^+ and Na^+ has been effective to adjust the profile of residual stresses near the free surface [7–10, 13, 15–17]. In a single ion-exchange process, compressive residual

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stresses exist on the glass surface if K^+ is diffused into the glass structure to substitute Na^+; conversely, tensile residual stresses arise if Na^+ replaces K^+. However, in a two-step ion-exchange process, or in a so-called double ion-exchange process, the distributions of residual stresses become very complicated. In a double ion-exchange process, if K^+ is first diffused into the glass structure to substitute Na^+ and then Na^+ is back diffused to partially replace K^+, a maximum compressive residual stress is supposedly located at the glass subsurface. The magnitude and the location of this maximum compressive stress are crucial for the glass flaw-insensitivity. Therefore, through ion-exchange methods for obtaining excellent mechanical properties or flaw-insensitivity, glasses are required to have interchange behaviors of Na^+ and K^+.

Whether a glass in the SiO_2–Al_2O_3–Na_2O–K_2O system has ion-exchange behavior is dependent on the composition. For example, glasses with a molar fraction of $(K_2O + Na_2O)/Al_2O_3 = 1$ do not have any ion-exchange behavior of K^+ and Na^+, because of no non-bridging oxygen in the glass structure [18]. However, these glasses have good chemical durability in the oral environment [14]. For obtaining the appropriate ion-exchange behaviors, and also without sacrificing chemical durability significantly, silicate glasses with the composition of $(0.2K, 0.8Na)_2O–xAl_2O_3–ySiO_2$ ($x = 0.4$–0.8, $y = 4$–6) were chosen for study. By using the above two advantages, one can obtain dental glass ceramics for systematically evaluating their mechanical properties after different ion-exchange practices.

Most commercial glasses are directly manufactured from the molten liquid, and then are fabricated into different shapes, such as rod and plate [7–10]. However, dental glass ceramics are mainly processed from the powder-sintering technique. Glasses with the same composition are expected to have different flaws or defects if they are fabricated through different processes. Although the silicate glass investigated by Green et al. has a flaw-insensitivity behavior, dental glass ceramics with the same composition are required to evaluate their mechanical properties again when they are obtained from different processes. In this study, through the powder-sintering technique, silicate dental glasses with the composition of $(0.2K, 0.8Na)_2O–xAl_2O_3–ySiO_2$ ($x = 0.4$–0.8, $y = 4$–6) are used to systematically observe the relationships between mechanical properties and ion-exchange processes.

Experimental procedures

The starting powders were SiO_2 (99.9% pure, Alfa), Al_2O_3 (99.9% pure, Alfa), Na_2CO_3 (99.5% pure, Aldrich), and K_2CO_3 (99% pure, Aldrich). These powders were proportionally mixed with isopropyl alcohol, according to the specific composition of $(0.2K, 0.8Na)_2O–xAl_2O_3–ySiO_2$ ($x = 0.4$–0.8, $y = 4$–6) listed in Table 1. After being well mixed inside the porcelain jar, each powder/alcohol solution was dried to remove isopropyl alcohol. A batch of the dried powders was heated, up to 1,050–1,100 °C for 0.5 h, to form a molten liquid in the platinum crucible. Subsequently, the molten liquid in the platinum crucible was brought out from the furnaces, and was directly air-quenched to obtain glass at room temperature. The quenched glass was then ground, and wet ball-milled with isopropyl alcohol inside an Al_2O_3 jar, by using Al_2O_3 balls as grinding media. After the alcohol was removed from the slurry, the dried powders were sieved to collect fine powders with the particle size <75-mesh for powder packing.

A batch of 13 g fine glass powders was mixed with isopropyl alcohol. The mixed powder/alcohol slurry was then poured into a rectangular stainless steel die, in which the inner dimensions were $28(W) \times 84(L)$ mm^2. After naturally dried at room temperature, these powders were cold-pressed to form a green powder-

Table 1 Fusion and sintering temperatures of different silicate glass ceramics

Material	Chemical formula	Composition (mol)					T_f (°C)[a]	T_s (°C)[b]
		SiO_2	Al_2O_3	Na_2O	K_2O	MgO		
SA1	$(0.8Na,0.2K)_2O \cdot Al_2O_3 \cdot 4SiO_2$	0.200	0.050	0.040	0.010	0.000	1,050	900
SA2	$(0.8Na,0.2K)_2O \cdot 0.8Al_2O_3 \cdot 4SiO_2$	0.200	0.040	0.040	0.010	0.000	1,050	900
SA3	$(0.8Na,0.2K)_2O \cdot 0.6Al_2O_3 \cdot 4SiO_2$	0.200	0.030	0.040	0.010	0.000	1,000	850
SA4	$(0.8Na,0.2K)_2O \cdot 0.4Al_2O_3 \cdot 4SiO_2$	0.200	0.020	0.040	0.010	0.000	900	750
SB1	$(0.8Na,0.2K)_2O \cdot Al_2O_3 \cdot 5SiO_2$	0.250	0.050	0.040	0.010	0.000	1,050	900
SB2	$(0.8Na,0.2K)_2O \cdot 0.8Al_2O_3 \cdot 5SiO_2$	0.250	0.040	0.040	0.010	0.000	1,000	900
SB3	$(0.8Na,0.2K)_2O \cdot 0.6Al_2O_3 \cdot 5SiO_2$	0.250	0.030	0.040	0.010	0.000	1,000	850
SC1	$(0.8Na,0.2K)_2O \cdot Al_2O_3 \cdot 6SiO_2$	0.300	0.050	0.040	0.010	0.000	1,050	900
SC2	$(0.8Na,0.2K)_2O \cdot 0.8Al_2O_3 \cdot 6SiO_2$	0.300	0.040	0.040	0.010	0.000	1,000	850
SC3	$(0.8Na,0.2K)_2O \cdot 0.6Al_2O_3 \cdot 6SiO_2$	0.300	0.030	0.040	0.010	0.000	900	800
SC4	$(0.8Na,0.2K)_2O \cdot 0.4Al_2O_3 \cdot 6SiO_2$	0.300	0.020	0.040	0.010	0.000	900	750

[a] T_f, fusion temperature; [b] T_s, sintering temperature

compact under a uniaxial compressive stress of 17 MPa inside the stainless steel die. The green powder-compact was then sintered at 750–900 °C for 1 h, with a heating rate of 2 °C/min. Sintering temperature for the green powder-compact approximately increased with the increasing Al_2O_3 or SiO_2 content of the green powder-compact, as listed in Table 1. After sintering, each densified cake was cut into 15–16 test bars. The dimensions of each test bar were $25(L) \times 4(W) \times 3(T)$ mm^3 approximately. All test bars were chamfered and then surface-polished by Al_2O_3 powders down to 0.05 μm. After polishing, these test bars were annealed to remove residual stresses at 650 °C for 0.5°h. The annealed specimens were then subjected to different ion-exchange processes. In a single ion-exchange process, specimens were soaked in the molten KNO_3 bath at 350–450 °C for 20 h. In a double ion-exchange process, specimens were first soaked in the molten KNO_3 bath at 350–450 °C for 20 h, and then were dipped into the molten $KNO_3/NaNO_3$ (2:1) bath at 350–450 °C for 0.5 h to obtain another ion-exchange treatment. As to the hydration treatment, specimens were soaked in a 4% acetic aqueous solution at 85 °C for 20 h.

Mechanical properties of the ion-exchange specimens were measured by a four-point bending method. The bending test was operated at room temperature by an Instron testing machine, with a crosshead speed of 0.6 mm/min. A four-point bending fixture with an inner span 10 mm and an outer span 20 mm was used. Phase existence was determined by X-ray diffractometry (XRD; Rigaku Co., Ltd., Tokyo, Japan) at room temperature, with a scanning speed of 2°/min. Scanning electron microscopy (SEM; Model S-2700, Hitachi Co., Ltd., Tokyo, Japan) was used to observe the fractographs of sintered glasses, and also to determine the concentration of K^+ or Na^+ along the thickness direction. A fresh dry-cutting surface or a fresh fracture surface was used to observe the concentration of K^+ or Na^+ along the thickness direction, for avoiding any other contamination.

Results and discussion

Phase existence

X-ray diffraction patterns of the sintered glasses are shown in Figs. 1 and 2. The data indicated that the silicate glasses with $n_{SiO_2} = 4$, the molar number of SiO_2 in the chemical formula listed in Table 1, did not contain any crystalline phase, but the silicate glasses with $n_{SiO_2} = 6$ contained a crystalline feldspar phase, orthoclase. Apparently, different ion-exchange processes did not affect the phase existence or the crystalline phase in these glasses. Overall, the crystalline phase in these silicate-containing glasses was mainly affected by the initial composition, not by the ion-exchange processes.

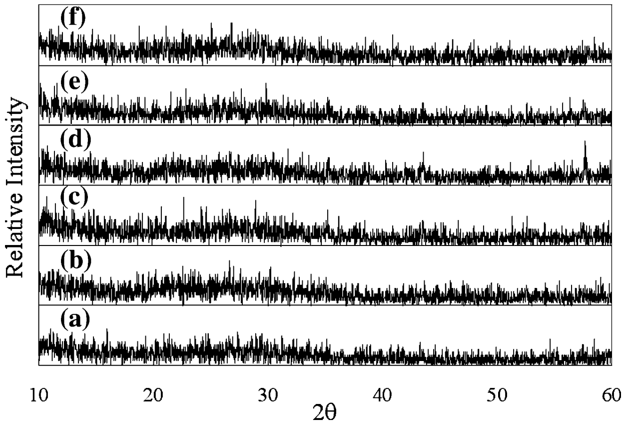

Fig. 1 X-ray diffraction patterns for (**a**) sample SA4 after a double ion-exchange, (**b**) as-annealed sample SA4, (**c**) sample SA3 after a double ion-exchange, (**d**) as-annealed sample SA3, (**e**) sample SA2 after a double ion-exchange, and (**f**) as-annealed sample SA2

Mechanical properties

Glasses with the ion exchanges of K^+ and Na^+

Flexural strength of different ion-exchange specimens is listed in Table 2. Among three different groups of samples, the single ion-exchange specimens had the

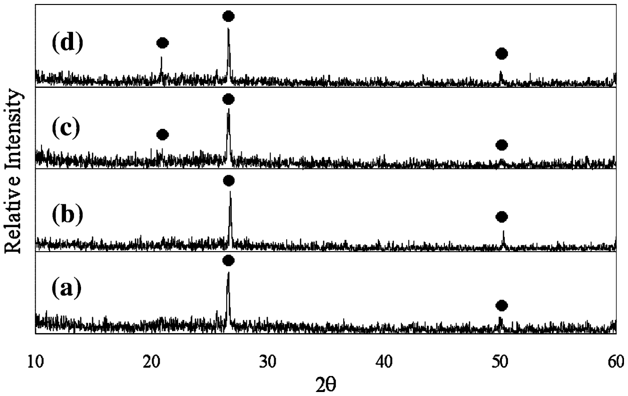

Fig. 2 X-ray diffraction patterns for (**a**) sample SC4 after a double ion-exchange, (**b**) as-annealed sample SC4, (**c**) sample SC3 after a double ion-exchange, and (**d**) as-annealed sample SC3. Symbol (•) is for the diffraction peaks of the orthoclase phase, $KAlSi_3O_8$

Table 2 Flexural strength for samples with different ion exchanges

Material	Flexural strength (Mpa)		
	As annealed[a]	After a single ion-exchange[b]	After a double ion-exchange[c]
SA2	89.3 ± 9.1	188.1 ± 39.6	–
SA3	50.5 ± 1.2	98.5 ± 7.4	97.9 ± 12.9
SA3	73.1 ± 6.6	118.8 ± 7.8	128.9 ± 7.5
SA4	83.3 ± 13.2	140.9 ± 3.4	103.8 ± 0.8
SC2	59.5 ± 4.7	81.9 ± 9.9	100.8 ± 1.8
SC3	88.2 ± 21.0	144.1 ± 52.9	141.3 ± 20.2
SC4	95.6 ± 12.0	177.9 ± 26.2	160.8 ± 3.5

[a] Annealed at 650 °C for 0.5 h; [b]ion-exchanged in K_2NO_3 bath at 450 °C for 20 h; [c]first ion-exchanged in K_2NO_3 bath at 450 °C for 20 h, and then in $(K,Na)_2NO_3$ at 400 °C for 0.5 h

highest flexural strengths, but the as-annealed specimens had the lowest. However, the standard deviation of flexural strength in the double ion-exchange specimens was slightly lower than that in the other two groups of samples. The same order of the standard deviation in flexural strength had been reported in the previous studies [8–10].

Weibull plots for different double ion-exchange materials are shown in Figs. 3–5. Related mechanical properties of these specimens are summarized in Table 3. Specimens with a double ion-exchange process at 350 °C had higher flexural strength than those at 400 °C. This phenomenon became significant for the specimens with a composition of $(0.8Na, 0.2K)_2O \cdot 0.4Al_2O_3 \cdot 4SiO_2$, because these specimens had a much lower glass transition temperature. With a lower glass transition temperature, specimens with a double ion-exchange process at 400 °C had a tendency toward higher stress relaxation during the ion-exchange process. Therefore, these samples had much lower flexural strength, approximately 40% lower, than those ion-exchanged at 350 °C.

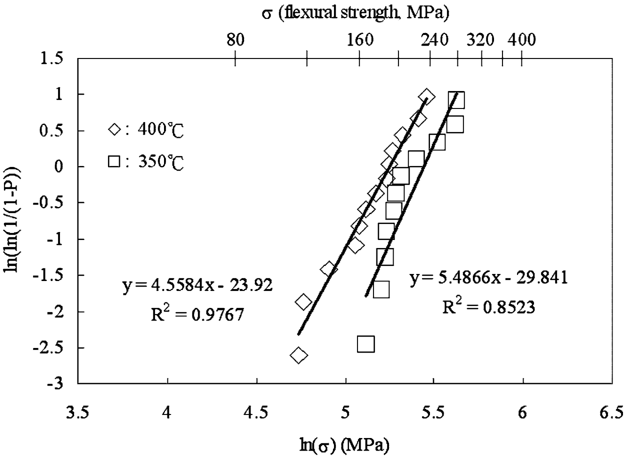

Fig. 4 Weibull plots for sample SA2 after a double ion-exchange at *T* = 400 °C and at *T* = 350 °C, respectively

From the data listed in Table 3, the Weibull modulus (m) in the double ion-exchange specimens was 5–8, which was much smaller than that in the commercial silicate glasses [8–10]. From SEM micrographs shown in Fig. 6, it was revealed that these double ion-exchange specimens had some large defects up to 30 μm. These large defects were expected to affect the mechanical properties of these double ion-exchange specimens. From electron dispersive X-ray spectrum analysis (EDXS), the concentration distributions of K^+ and Na^+ along the thickness direction for a double ion-exchange specimen are shown in Fig. 7. The maximum concentration of K^+ was located at ~20 μm below the surface, which was probably the locus of maximum

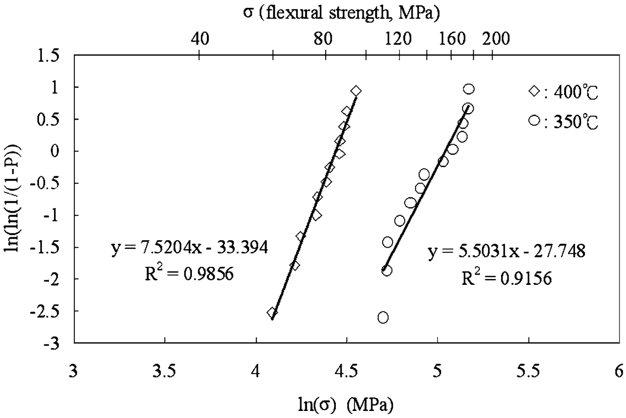

Fig. 3 Weibull plots for sample SA4 after a double ion-exchange at *T* = 400 °C and at *T* = 350 °C, respectively

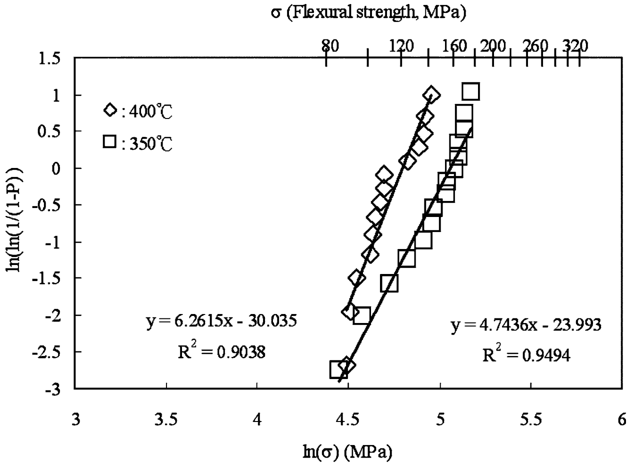

Fig. 5 Weibull plots for sample SC4 after a double ion-exchange at *T* = 400 °C and at *T* = 350 °C, respectively

Table 3 Flexural strength and the Weibull modulus for double ion- exchange specimens

Material	Ion-exchange temperature (°C)	MOR (MPa)[a]	m[b]
SA4	400	80.0 ± 8.3	7.5
SA4	350	134.0 ± 27.6	5.5
SA2	400	173.9 ± 29.6	4.6
SA2	350	213.0 ± 31.0	5.5
SC4	400	106.6 ± 15.5	6.3
SC4	350	144.1 ± 22.0	4.7

[a] Modulus of rupture or flexural strength; [b]the Weibull modulus

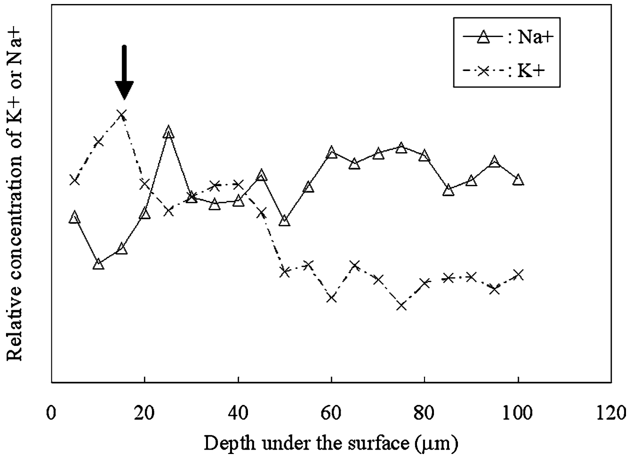

Fig. 7 The concentration distributions of cations K^+, Na^+ along the thickness direction for sample with a double ion-exchange process at 400 °C. The arrow symbol "↓" is used to point the possible locus of maximum compressive stress

compressive stress equivalently. With such a shallow locus of maximum compressive stress, not surprisingly the double ion-exchange samples in this study were still flaw-sensitive [7–10]. For further increasing mechanical reliability, dental glass ceramics should have either a flaw size as small as possible, or the locus of maximum compressive stress deep enough, which could be obtained from the appropriate powder-sintering techniques or double ion-exchange practices.

Glasses with a hydration treatment

Flexural strength of different hydrated specimens is listed in Table 4. These hydrated glasses had been heat-treated in a 4% acetic acid solution at 85 °C for 20 h. The hydrated specimens had higher flexural strength than those without hydration. The strengthening mechanism of the hydrated glasses was believed not directly from the ionic size effect, because H^+ was much smaller than Na^+ and K^+. The strengthening mechanism of these hydrated glasses is probably from the modification of surface flaws or other effects. A recent study has reported that the strengthening mechanism of one acetic-acid-treated dental glass was due to the modification of surface flaws, but not from hydroxyl ions [19]. The OH^- bonds were not being observed increasing in the surface of this particular acetic-acid-treated dental glass. However, the silicate glasses in this study are designed to have various degrees of ion exchanges between H^+, Na^+, and K^+. Whether the OH^- bonds on the glass surface play an important role of strengthening mechanism for hydrated dental glasses are still under investigation.

Conclusion

Silicate-containing dental glass ceramics with the composition of $(0.2K, 0.8Na)_2O–xAl_2O_3–ySiO_2$ ($x = 0.4–0.8$, $y = 4–6$) were studied for their mechanical properties after different ion-exchange processes. Silicate glass ceramics were obtained at 750–850 °C by using the powder-sintering technique. Sintered glasses were soaked at 350–450 °C in molten KNO_3 or $NaNO_3 + KNO_3$ salt baths for a single or a double ion-exchange process of Na^+ and K^+ cations. Except for the ion interchanges of Na^+ and K^+, the sintered or ion-exchanged specimens were also soaked in a 4% acetic acid at 85 °C for a hydration treatment. Glass ceramics with the composition of $(0.2K, 0.8Na)_2O–$

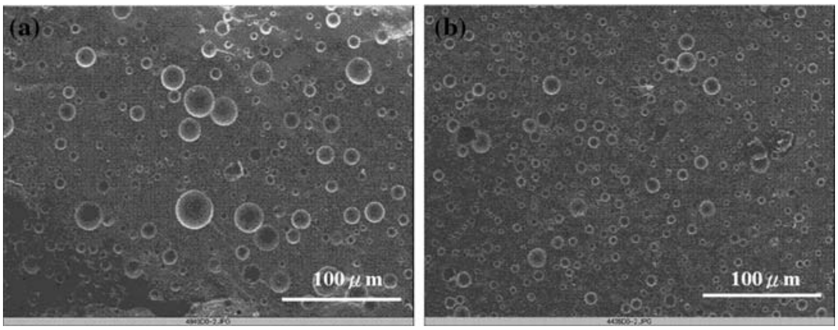

Fig. 6 SEM micrographs for (**a**) sample SA2, and (**b**) sample SA4 after a double ion-exchange at 350 °C

Table 4 Flexural strength for samples with or without a hydration treatment

Material	Flexural strength (MPa)			
	As-annealed[a]	After hydration	After a single ion-exchange[b]	After a single ion-exchange + hydration[c]
SA4	–	–	137.5 ± 22.1	150.7 ± 18.6
SC4	78.2 ± 8.0	86.4 ± 8.6	149.8 ± 25.2	–
SC4	69.8 ± 5.1	88.7 ± 13.5	–	–

[a] Samples annealed at 650 °C for 0.5 h; [b]ion-exchanged in the K_2NO_3 bath at 350 °C for 90 h; [c]first ion-exchanged in K_2NO_3 bath at 350 °C for 90 h, and then hydrated in the 4% acetic acid aqueous solution at ~85 °C for 20 h. At least 3–7 test bars for each sample

xAl$_2$O$_3$–6SiO$_2$ ($x = 0.4$–0.8) contained a feldspar crystalline phase, orthoclase, which was apparently not affected by the different ion-exchange processes. Therefore, the crystalline phase in the silicate-containing glasses was mainly controlled by the initial composition, not by the ion-exchange processes.

Different ion-exchange processes significantly affected the mechanical properties of silicate-containing dental glasses. As to flexural strength, the double ion-exchange specimens were slightly lower than the single ion-exchange specimens, but much higher than the as-annealed specimens. Flexural strength for double ion-exchange specimens increased with decreasing ion-exchange temperature. Some double ion-exchange specimens had found their flexural strength up to 280 MPa. However, the Weibull modulus of these double ion-exchange groups was 5–8, smaller than most commercial glass, because of the presence of defects larger than 30 μm. For further increasing mechanical reliability, the double ion-exchange specimens were required to have smaller flaws or appropriate double ion-exchange practices. Specimens with a hydration treatment had higher flexural strength than those without it. The strengthening mechanism of hydrated samples is still under investigation.

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