



Structural modifications induced by Na⁺/K⁺ ion exchange in silicate glasses: A multinuclear NMR spectroscopic study



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ABSTRACT

The structural mechanisms of stress relaxation during Na⁺/K⁺ ion exchange is studied in a variety of Na silicate glasses with and without alkaline-earth modifiers, using one and two-dimensional ²³Na and ²⁹Si nuclear magnetic resonance (NMR) spectroscopy. The results suggest that significant structural modifications accompany the Na⁺/K⁺ ion exchange process in the form of a shortening of the average Na–O and Si–NBO distances and an opening of the Si–O–Si angles without any detectable change in the Qⁿ speciation. These trends are similar to those observed in analogous mixed Na,K glasses derived via the melt-quench route, with increasing K:Na ratio. Consequently, the ion-exchange-induced reorganization of the glass network is accompanied by a partial relaxation of the stress generated by the exchange of smaller Na⁺ by the larger K⁺ and better accommodation of the latter ion as a modifier.

1. Introduction

A major limitation in many technological applications of glassy materials is their brittle fracture behavior [1]. However, exchanging smaller ions such as Na⁺ in the glass structure with larger ions such as K⁺ leads to chemical strengthening, as it allows for developing high surface compressive stress, which in turn drastically improves the modulus of rupture of the treated glass [2]. The magnitude of this surface compressive stress depends on the extent of stress and structural relaxation occurring during the ion exchange [2,3]. Therefore, the optimization of the ion-exchange process requires a fundamental understanding of the nature of this relaxation process [3].

Varshneya et al. used molecular dynamics (MD) simulation to study the buildup and relaxation of stress during ion exchange in a 75SiO₂-15Na₂O-10CaO glass [2,4] and postulated that the response of the glass structure to the Na⁺/K⁺ ion exchange can be separated into multiple stages [2]. The K⁺ ions being larger than Na⁺, there is an initial buildup of stress as the former replaces the latter in the glass structure. This stage is followed by several successive steps of stress relaxation. The first relaxation step involves an increase of the K–NBO distances which expands the volume of the nearest-neighbor coordination sphere to better accommodate the K⁺ ions. This step is followed by a “fast β-process of delayed elastic stress relaxation” that involves alkali diffusion in the glass network. The next step is the “slow irreversible α stress

relaxation” that involves changes in the Si–O network topology. The last relaxation step is the structural relaxation appearing when there is no more stress in the glass. During this step, which may last years, the network undergoes long-range cooperative structural relaxation in order to achieve the structure of the melt-quenched glass of same composition [2].

Although such a model of multi-stage structural relaxation appears to be intuitively correct, significant controversy remains regarding the nature and even the existence of changes in the Si–O network topology for ion exchange process realized at temperatures significantly below the nominal glass transition temperature T_g where the silicate network is expected to remain practically “frozen” at experimental timescales [5]. This hypothesis is in contradiction with the proposal of Ingram et al. [6] who conjectured that the Si–O network may respond even below T_g via a change in the Qⁿ speciation (e.g. Q₂ + Q₄ ⇌ 2Q₃) during the ion-exchange process, in order to accommodate the arrival of K⁺ cations in the ion-exchanged glass. However, MD simulation results reported by Tandia et al. [1] and Kreski et al. [7] indicated no detectable change in Qⁿ speciation accompanying ion exchange in silicate glasses.

Here, we report the results of a ²³Na and ²⁹Si nuclear magnetic resonance (NMR) spectroscopic study of the atomistic details of the structural adaptation of the host modifier cation and the Si–O network in binary Na-silicate and ternary Na,Mg-, Na,Ba- and Na,Ca-silicate

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Table 1

Analyzed chemical compositions (in mol%) of glasses produced for ion-exchange process and their respective T_g (°C).

Sample	SiO ₂	Na ₂ O	CaO	MgO	BaO	T_g
SN	78 ± 2	22 ± 2	0	0	0	502
SNC	64 ± 4	26 ± 4	10 ± 1	0	0	544
SNM	64 ± 1	27 ± 1	0	9 ± 1	0	511
SNB	74 ± 1	17 ± 1	0	0	9 ± 1	521

glasses following the Na⁺/K⁺ ion exchange. Although NMR spectroscopy is a powerful element-specific structural probe, owing to its relatively low sensitivity its application has remained limited to study bulk structure. This limitation poses a problem since ion exchange is typically limited to a depth of a few microns near the surface. In order to circumvent this problem, the ion exchange is performed on fine (few hundred μm) glass powder to maximize the volume fraction of the ion exchanged region.

2. Experimental method

2.1. Glass synthesis

The glass compositions that were ion-exchanged in this study are listed in Table 1. These four glasses were synthesized by typical melt-quench method from constituent oxide and carbonate precursors. The constituents were thoroughly mixed and decarbonated at 740 °C for about 15 h and were subsequently melted for 2 h in a platinum crucible at 1450 °C followed by quenching. The resulting glass samples were crushed and remixed followed by remelting for two additional hours to improve glass homogeneity. The final melts were quenched on a graphite plate and annealed for 12 h at the respective glass transition temperature T_g , in order to release the internal stresses. Each of the four glasses was doped with 0.1 wt% CoO to enhance the ²⁹Si spin-lattice relaxation rate to shorten the time required for data collection for two-dimensional (2D) ²⁹Si NMR spectroscopy at natural isotopic abundance. The chemical composition of these four glass samples was analyzed by X-ray fluorescence (XRF, Siemens Bruker S4 PIONEER, Cu Kα radiation) and is listed in Table 1, with the notation SN (C,M or B) where S is for silicon, N for sodium, C for calcium, M for magnesium and B for barium. Thermal analysis (DTA, Netzch STA 409 PC) was carried out to determine the T_g of these glasses. Measurements were performed under helium atmosphere on 40–50 mg of glass powder taken in alumina crucibles. The T_g was determined to within ± 2 °C, as the inflection of the glass transition region, using a heating rate of 25 °C/min (Table 1).

Additionally, several other glasses with similar modifier:silica molar ratio as these four glasses but with varying Na/(Na + K) ratio (see Table 2) were synthesized using identical procedure in order to analyze the effect of incorporation of K on the Na and Si environments in melt-quenched glasses and to compare that with the corresponding effects in the Na⁺/K⁺ ion exchanged analogues.

Table 2

Nominal compositions (in mol%) glasses produced to study the effect of the Na/Na + K ratio on the Na and Si environments.

SiO ₂	Na ₂ O	K ₂ O	CaO	MgO	BaO
75	18.75	6.25	0	0	0
75	12.5	12.5	0	0	0
75	6.25	18.75	0	0	0
65	18.75	6.25	10	0	0
65	12.5	12.5	10	0	0
65	6.25	18.75	10	0	0
65	18.75	6.25	0	10	0
65	12.5	12.5	0	10	0
65	6.25	18.75	0	10	0
75	7.5	7.5	0	0	10

2.2. Ion exchange process

The SN, SNM, SNC and SNB glasses were crushed and sieved to obtain particle sizes ranging between 850 and 1200 μm for the SN, SNM and SNC glasses, while for the SNB the particle size ranged between 200 and 300 μm. The crushed glass powders were placed in stainless steel bags with mesh size of 800 μm for the SN, SNM and SNC glasses, while this mesh size was 200 μm for the SNB glass. The SN glass was ion-exchanged for 24 h at 400 °C in a KNO₃ molten salt bath and the SNC, SNM and SNB samples were ion-exchanged for 66 h at 400 °C in the bath. The ion-exchanged powders were finally washed in water and subsequently used for NMR spectroscopic measurements (see below). For each composition a plate-shaped sample was prepared and ion-exchanged under identical conditions for measurement of K interdiffusion profiles (see below).

2.3. Interdiffusion characterization

The ion-exchanged plate-shaped samples were cut and the cross section was embedded in resin, polished down to 3 μm using abrasive polishing pads and cerium oxide. In order to avoid charging effect, these samples were coated with a thin carbon coating. The K profiles were obtained by performing line scans from the surface to a desired depth in the material using an energy dispersive X-ray spectrometer in a scanning electron microscope (FEG-SEM, Hitachi SU 70). The measurements were performed with an accelerating voltage of 15 kV and a dwell time of 1 s, using 1 cm² solid-state detector.

2.4. NMR spectroscopic measurements

2.4.1. ²³Na NMR spectroscopy

²³Na magic-angle-spinning (MAS) NMR measurements were carried out on SN, SNC and SNM glasses and their mixed-ions (Na + K) analogues at 11.7 T using a Bruker Avance500 spectrometer operating at a Larmor frequency of 132.3 MHz for ²³Na and a Bruker TR-MAS probe. Crushed glass samples were taken in a 4 mm ZrO₂ rotor and were spun at ~15 kHz. A solids π/10 pulse (0.25 μs) was used to selectively excite the central transition (+ 1/2 ↔ - 1/2) and a recycle delay of 0.5 s was used. Approximately 2400 FIDs were averaged and Fourier transformed to obtain each ²³Na MAS NMR spectrum. The ²³Na chemical shift was externally referenced to the isotropic chemical shift δ_{iso} of NaCl aqueous solution ($\delta_{iso} = 0$ ppm).

2.4.2. 2D ²⁹Si NMR spectroscopy

The effect of ion exchange on the Si–O network is investigated by probing the ²⁹Si chemical shift tensor in these glasses. It may be noted here that the principal components of the chemical shift tensor (δ_{xx} , δ_{yy} , and δ_{zz}) can be expressed in terms of the isotropic chemical shift δ_{iso} , the magnitude of anisotropy Δ , and the asymmetry parameter η , in accordance with the Haerberlen convention [8]. These terms are defined as:

$$\delta_{iso} = \frac{1}{3}(\delta_{zz} + \delta_{yy} + \delta_{xx}); \quad \Delta = \delta_{zz} - \delta_{iso}; \quad \eta = \frac{\delta_{xx} - \delta_{yy}}{\Delta} \quad \text{where,} \\ \delta_{zz} - \delta_{iso} \geq \delta_{xx} - \delta_{iso} \geq \delta_{yy} - \delta_{iso}.$$

Various Qⁿ species in the ²⁹Si NMR spectra of silicate glasses can be identified on the basis of their characteristic δ_{iso} . However, additional structural information regarding the site symmetry and conformation for the various Qⁿ species can be gained from determination of the anisotropy and the asymmetry of the chemical shift tensor. The 2D magic-angle-turning phase-adjusted-sideband-separation (MATPASS) NMR experiment is well suited for this purpose as it separates isotropic chemical shifts in one dimension while simultaneously separating the chemical shift anisotropy (CSA) for each isotropic shift in the form of a powder sideband pattern into a second dimension. The high field (19.6 T) 2D ²⁹Si MATPASS NMR experiments were performed on the parent and ion-exchanged SNB glass and its mixed-ions K-doped

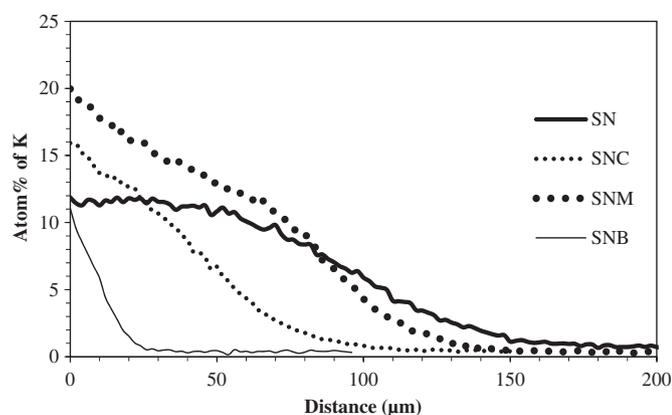


Fig. 1. K concentration as a function of depth in ion-exchanged SN, SNC, SNM and SNB glasses.

analogue SNB7.5K glass (75SiO₂-7.5Na₂O-7.5K₂O-10BaO) at the National High Magnetic Field Laboratory using an ultra-narrow bore magnet equipped with a Bruker DRX console operating at a resonance frequency of 165.2 MHz for ²⁹Si. Crushed glass sample was packed into a 3.2 mm ZrO₂ rotor and was spun at 5 kHz. The 2D MATPASS NMR data were collected with Car-Purcell-Meiboom-Gill (CPMG) echo-train acquisition to enhance sensitivity.

The pulse sequence used a series of five MAT π -pulses (4.0 μ s) with incremented inter-pulse delays according to the timings detailed by Hung et al. [9]. The method of States et al. [10] was used for hypercomplex data acquisition applied to the phases of the CPMG pulses and the receiver. Acquisition consisted of 16 hypercomplex t_1 points with 36 transients per point and with 140 CPMG echoes per transient and a recycle delay of 60s. The ²⁹Si chemical shifts were externally referenced to tetramethylsilane (²⁹Si δ_{iso} = 0 ppm).

3. Results

3.1. Interdiffusion properties

In Fig. 1, the potassium profiles for the ion-exchanged SN, SNM, SNC and SNB glasses are represented. The depth of interdiffusion ranges between 28 and 160 μ m. The SNB glass has the lowest depth of interdiffusion and atomic fraction of potassium at the surface due to the lower Na₂O content of the parent glass (Table 1). A comparison between the K profiles in SN, SNM and SNC glasses show that the SNM glass has the highest atomic fraction of K at the surface while the SN and SNB glasses have the lowest.

3.2. ²³Na NMR results

The ²³Na MAS NMR spectra of the parent and ion-exchanged SN, SNC, SNB and SNM glasses, as well as of the K-doped mixed-ions SN glass of composition 75SiO₂-12.5Na₂O-12.5K₂O (SN12.5K) and SNB (75SiO₂-7.5Na₂O-7.5K₂O-10BaO) are shown in Fig. 2. These spectral line shapes are all asymmetric with low frequency tails that are characteristic of the central transition line shape of quadrupolar nuclides in sites with a distribution of the quadrupolar coupling constant C_Q , likely resulting from structural disorder. These line shapes can be simulated well with a Czjzek distribution of the C_Q parameter. Such simulations have been carried out using the software DMFIT [11] and the resulting δ_{iso} and C_Q values are listed in Table 3. The average Na–O nearest-neighbor distances in these glasses were estimated from the ²³Na δ_{iso} using the relationship proposed by Stebbins and coworkers [12,13] for anhydrous silicates:

$$\delta_{iso} \text{ (ppm)} = -67(\text{Na} - \text{O} (\text{\AA})) + 179 \quad (1)$$

Besides Na-silicates, Eq. 1 has been found to also work well for Na and Na,K aluminosilicates in correctly predicting the relative changes in the average Na–O distances from ²³Na δ_{iso} [13,14]. Therefore, it is reasonable to assume the validity of Eq. 1 in the case of the mixed-modifier silicate glasses studied here. It is clear from Fig. 2 and Table 3 that although the ²³Na C_Q does not change significantly between different glasses, the ²³Na δ_{iso} consistently shifts to higher frequency (higher ppm) upon Na⁺/K⁺ ion exchange. This result, in conjunction with Eq. 1, implies a concomitant shortening of the Na–O distance in these glasses upon ion exchange (Table 3). The largest shift in ²³Na δ_{iso} between the exchanged and the parent glass is observed for the SN glass. Additionally, it is important to note that the ²³Na δ_{iso} of the SN12.5K glass shifts the most to higher frequency in comparison with both the parent and the ion-exchanged SN glasses (cf. Fig. 2(c)).

Finally, the evolution of the ²³Na δ_{iso} with the Na/(Na + K) ratio for the mixed-ions analogues of the SN, SNC and SNM glasses is shown in Fig. 3. It is clear that the ²³Na δ_{iso} shifts nearly linearly to higher frequency with increasing K content. Moreover, it appears that for any specific Na/(Na + K) content the ²³Na δ_{iso} in the mixed-ions glasses increases following the order SN(K)M > SN(K)C > SN(K) (Fig. 3).

3.3. ²⁹Si MATPASS/CPMG NMR results

The isotropic projections of the ²⁹Si MATPASS/CPMG NMR spectra of the parent and ion-exchanged SNB (75SiO₂-15Na₂O-10BaO) glasses as well as that of the melt-quenched mixed-ions analogue SNB7.5K glass (75SiO₂-7.5Na₂O-7.5K₂O-10BaO) are shown in Fig. 4. These spectra are characterized by two partially resolved resonances centered at ~ -93 and -105 ppm, corresponding, respectively, to the Q³ and Q⁴ environments in the glass structure and can be simulated well (Fig. 4) with two Gaussian peaks. The simulation parameters are listed in Table 4. The relative fractions of the as obtained from the constituent peak areas in these simulations agree well with the values expected from the nominal glass compositions.

It is clear from Table 4 that there is no detectable change in Qⁿ speciation upon ion exchange in the SNB glass. More interestingly, the ²⁹Si δ_{iso} of the Q³ and Q⁴ environments are shifted significantly to lower frequency (lower ppm) values for the ion-exchanged SNB and the mixed-ions SNKB glasses in comparison with those for the parent SNB glass (Fig. 4, Table 4).

The ²⁹Si anisotropic powder sideband patterns for the Q³ environment in these glasses on the other hand do not show any significant change (Fig. 5). This observation is not surprising since previous studies of the CSA of Q³ environments in silicate glasses indicated a linear dependence of this parameter with the field strength (FS) of the modifier cation [15], defined as Z/r^2 , where Z is the charge and r is the cation-oxygen distance which does not vary enough between Na⁺ (FS = 0.18) and K⁺ (FS = 0.12) to be observed with this experimental technique [16].

4. Discussion

4.1. Na⁺/K⁺ ion exchange: evolution of the modifier environment

The ²³Na NMR results, when taken together, clearly demonstrate that the observed shortening of the Na–O nearest neighbor distance in SN, SNM and SNC glasses upon ion exchange is similar to the effect of progressive addition of K to these glasses via the melt-quench route. There are two possible origins of this effect in the ion exchanged glasses. The first one is elastic and is related to the effect of the compressive stress developed in the structure due to the Na⁺/K⁺ ion exchange. The compressive stress arising from the ion-exchange may be compared to the compression of the glass at low temperature and relatively low pressure (≤ 2 GPa). In a recent in situ high-pressure ²³Na NMR study Gaudio et al. [14] have shown that the compression of al-bite glass at relatively low pressure (≤ 2 GPa) induces a shortening of

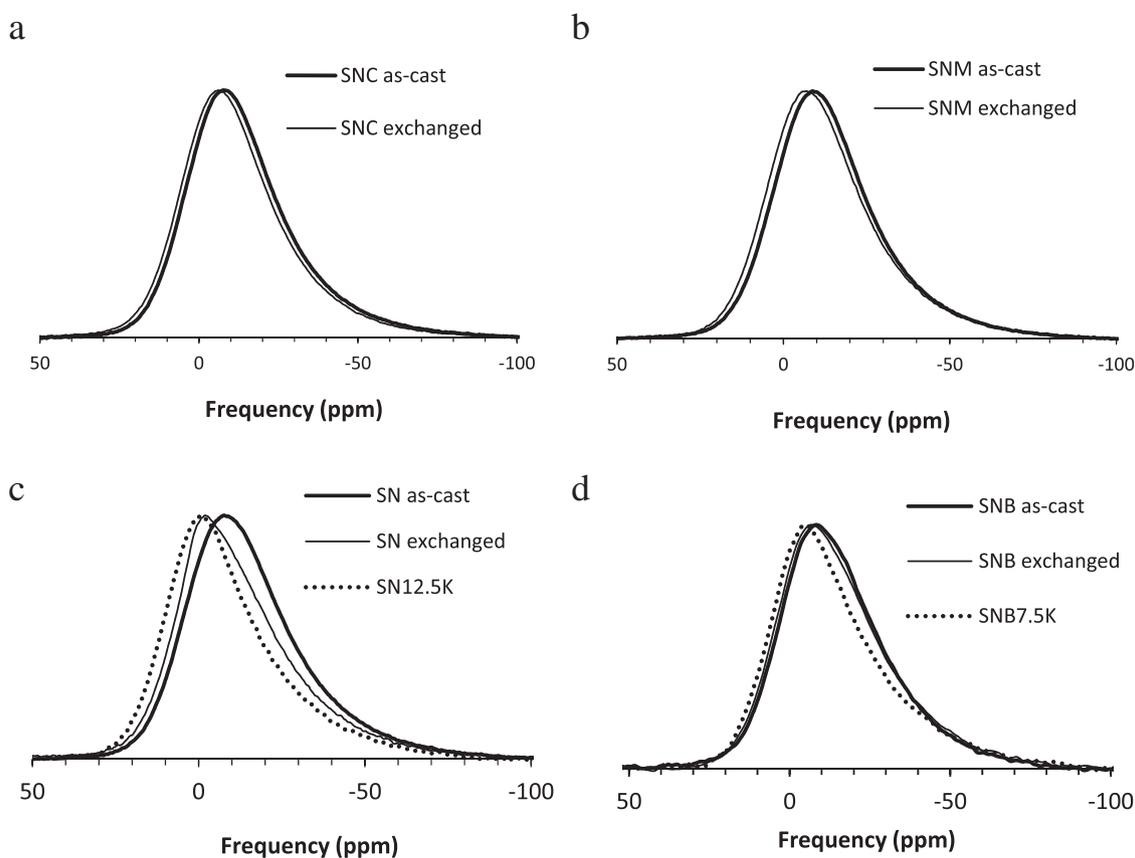


Fig. 2. Experimental ^{23}Na MAS-NMR spectra for the as-cast and ion-exchanged SNC (a), SNM (b), SN (c), SNB (d) glasses and the as-cast SN12.5K glass (c) and the as-cast SNB7.5K (d).

Table 3

Isotropic chemical shift (ppm), quadrupolar coupling constant (C_Q) and the Na–O distances obtained from the ^{23}Na NMR spectra for as cast and ion-exchanged SNC, SNM, SNB and SN and for the as-cast K-doped SN12.5K glass and SNB7.5K.

Glass	Isotropic chemical shift (± 0.2 ppm)	Na–O distances (\AA)	C_Q (± 0.1 MHz)
SNC as-cast	4.9	2.60	3.3
SNC exchanged	5.8	2.58	3.3
SNM as-cast	3.6	2.62	3.3
SNM exchanged	4.5	2.60	3.3
SN as-cast	4.2	2.61	3.0
SN exchanged	8.5	2.54	3.3
SN12.5K	10.1	2.52	3.2
SNB as-cast	2.9	2.63	3.3
SNB exchanged	4.8	2.60	3.4
SNB7.5K	7.2	2.56	3.4

the Na–O distance without any change in the coordination number of the network-forming Si and Al cations [14].

In fact, a reduction of the Na–O bond distance by ~ 0.06 \AA was observed between an uncompressed glass and one compressed at ~ 2 GPa at 300 K [14]. In the present study a reduction of ~ 0.064 \AA is observed between the parent and the partially ion-exchanged SN glass (Table 3). However, given the long treatment time of 24 h at 400 $^\circ\text{C}$ and the composition of the SN glass, it is unlikely that the ion-exchange-induced compressive stress in this glass is on the order of 2 GPa. Indeed, a compressive stress of ~ 1 GPa was observed in a glass of composition $70\text{SiO}_2\text{-}15\text{Na}_2\text{O-}10\text{CaO-}5\text{Al}_2\text{O}_3$ chemically exchanged at 400 $^\circ\text{C}$ for 8 h and alumina is known to improve the compressive stress level in Na^+/K^+ exchanged glasses [17]. Therefore, the extent of reduction of the Na–O bond distance observed in the present study between the parent and partially ion-exchanged SN, SNM and SNC glasses is too high to be due to the compressive stress developed during the ion-exchange

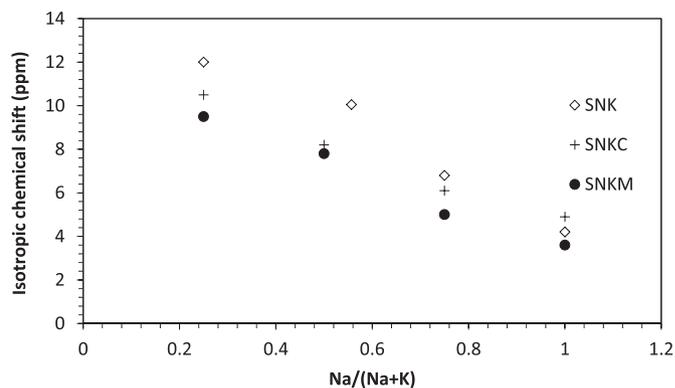


Fig. 3. ^{23}Na isotropic chemical shift as a function of the $\text{Na}/(\text{Na} + \text{K})$ ratio for the SN, SNM and SNC glasses.

process. A more conclusive evidence in favor of this hypothesis comes from the consideration of the relative volume of the ion-exchanged region in these glass particles. Under the assumption of spherical particle shape, calculations for an average particle size of 1000 μm and a K^+ penetration (case) depth of ~ 100 μm (Fig. 1) yield the volume of the ion-exchanged region to be about the same as that of the unexchanged core of these particles. Therefore, the compressive stress in the ion-exchanged region will be balanced by a comparably large tensile stress per unit volume in the core region. Since the NMR measurements are realized on the entire particle, such measurements should also probe the structural modifications induced by this tensile stress and the effects of comparable compressive and tensile stress per unit volume should cancel each other for each particle. However, as mentioned above, the ^{23}Na NMR results clearly indicate a significant shortening of the Na–O distances upon ion-exchange in all glasses. Moreover, the

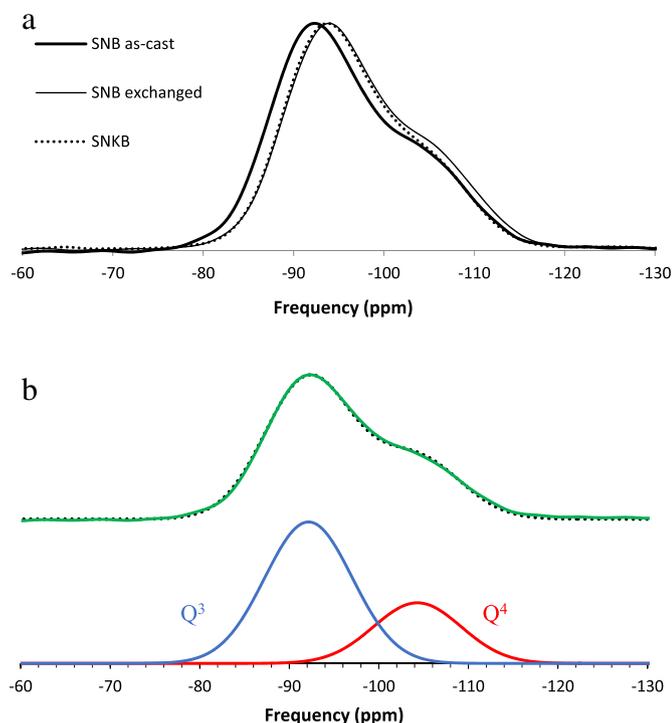


Fig. 4. Isotropic ^{29}Si 2D MATPASS spectra of the as-cast and ion exchanged SNB and the as-cast SNKB (75SiO₂-7.5Na₂O-7.5K₂O-10 BaO) glasses (A). Simulation (black dots) of the isotropic ^{29}Si 2D MATPASS spectrum (green line) of as-cast SNB glass. Individual Gaussian simulation components corresponding to the Q³ (blue curve) and Q⁴ (red curve) species (B). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

core region under tensile stress should relax more efficiently, owing to the more open character of the structural network in this region. Therefore, the observed Na–O bond distance reduction is quite unlikely to arise from any elastic effect of the stress induced by the ion-exchange process. Rather, we believe that an important contributor to the Na–O bond distance reduction is a stress/structural relaxation process that follows ion-exchange. It is clear from Fig. 3 that the Na–O bond distance in melt-quenched mixed Na–K SN, SNC and SNM glasses progressively decreases with increasing K content. Similarly, if the introduction of K via ion-exchange is followed by stress relaxation, then a contraction of the Na–O coordination shell in the ion-exchanged glass (and possibly a concomitant increase in the size of the K–O coordination shell) would lead to a reduction of the stress level. This scenario is consistent with the hypothesis of the “fast delayed-elastic stress relaxation” developed by Varshneya et al. [2]. These authors postulated that the alkali cations could jump from one ion cage into another during the ion-exchange process in order to relax the developed compressive stress. Hence, the Na⁺ in the glass, during ion-exchange would preferentially jump in smaller ion cages to enable the K⁺ to occupy the larger cages available and thereby relax the stress. This stress relaxation mechanism would be expected to result in Na–O coordination environments in ion-exchanged glasses that are similar to those in their

Table 4

Isotropic chemical shift, peak width and relative fraction (x) for each of the constituent Qⁿ species in parent and ion-exchanged SNB and melt-quenched SNKB glasses.

	Q ³			Q ⁴		
	δ_{iso} (± 0.1 ppm)	Width (ppm)	x (± 0.02)	δ_{iso} (± 0.1 ppm)	Width (ppm)	x (± 0.02)
SNB as-cast	–92.2	11.5	0.70	–104.3	11.5	0.30
SNB exchanged	–93.6	11.5	0.70	–105.4	11.5	0.30
SNKB as-cast	–93.5	11.5	0.72	–104.6	11.5	0.28

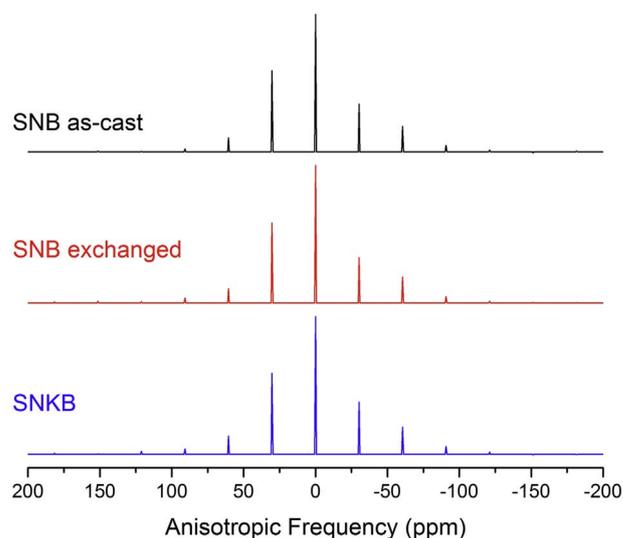


Fig. 5. Anisotropic projection of the Q³ environments in the ^{29}Si 2D MATPASS spectra of as-cast and ion exchanged SNB and the as-cast SNKB glasses.

melt-quenched analogues as is indeed observed here.

This scenario is also consistent with the fact that the largest shift in ^{23}Na δ_{iso} and consequently, the largest contraction in the Na–O distance (Fig. 2), between the exchanged and the parent glass is observed for the SN glass which indeed has the lowest T_g value and hence, the most thermal relaxation (cf. Table 1). This hypothesis is corroborated by the rather flat K⁺ diffusion profile (Fig. 1) for the SN glass.

4.2. Na⁺/K⁺ ion exchange: the network adaptation

The ^{29}Si NMR spectra of the SNB glass does not display any detectable change in the Qⁿ speciation upon ion exchange, a result that contradicts the claims of the observation of Q-species disproportionation made in a number of previous studies [18–20]. The absence of any detectable Q-species disproportionation may not be surprising considering the fact that the SNB glasses were ion-exchanged in the present study at ~ 120 °C below T_g where the shear viscosity is rather high and consequently the structural relaxation rate is significantly longer than the ion-exchange timescale. However, this does not explain the disagreement with the claims made in previous Raman spectroscopic studies of the observation of Q-species disproportionation in glasses that were Na⁺/K⁺ or Li⁺/K⁺ ion-exchanged even at temperatures as low as ~ 100 – 200 °C below T_g [18–20]. Rather this disagreement may point towards the possibility of change in the Raman scattering cross-sections of various Q-species upon the Na⁺/K⁺ ion-exchange process.

On the other hand, the ^{29}Si δ_{iso} of the Q³ environment in both the ion-exchanged SNB and the mixed-ions SNKB glasses shifts to lower frequency values by similar magnitude compared to that in the case of the parent SNB glass. This change may be related to a shortening of the Si–NBO distance in the ion-exchanged and mixed-ions melt-quenched glasses, NBO being the non-bridging oxygen on the Q³ unit [15]. This shortening may be explained by the higher field strength of Na⁺ in

comparison with K^+ . Indeed, the Na^+ will have a stronger pull on NBO compared K^+ and hence, the Si–NBO distance in Na-silicate glasses would be expected to be longer than that in K-silicate glasses. Moreover, the ^{29}Si δ_{iso} of the Q^4 environments is also shifted to lower frequency values for the ion exchanged SNB glass compared to the parent SNB glass and this shift is higher for the ion exchanged glass than for the mixed-ions SNKB glass. This shift likely corresponds to an increase in the Si–O–Si inter-tetrahedral bond angle due to the ion exchange process [12,21]. Indeed, an increase of the Si–O–Si inter-tetrahedral bond angle may be associated with a reorientation of the tetrahedral SiO_4 units in order to accommodate the presence of large K^+ cations. This result is consistent with a molecular dynamic simulation study of Kreski et al. [7] in Na^+/K^+ ion exchanged Na-silicate glass. Both a shortening of the Si–NBO distance and an opening of the Q^4 Si–O–Si angle would facilitate incorporation of K^+ in large K–O cages in the glass structure during ion exchange. Finally, it may be noted that a shift of the ^{29}Si δ_{iso} in the same direction for the Q^3 and Q^4 environments is also well documented in the literature for binary Na-silicate and K-silicate glasses with identical silica content [21]. Therefore, the ^{29}Si NMR results obtained in this study are consistent with the scenario that significant stress/structural relaxation follows the Na^+/K^+ ion exchange, even significantly below T_g , which tends to modify the structural network in a direction similar to that of a melt-quenched glass containing Na and K.

These results are in contrast with the conclusions drawn by Calahoo et al. [18] in a recent micro-Raman spectroscopic study of a Li^+/K^+ ion-exchanged silicate glass where they suggested a Si–O–Si bond angle reduction for the Q^2 and Q^3 species while a lengthening of the Q^4 Si–O bonds. This difference in the network adaptation between the present study and that of Calahoo et al. may be related to the difference in the stress state of the glass samples. In the present study the network modifications are a response to stress/structural relaxation in the small particles while in Calahoo et al.'s study the ion-exchanged layer in the bulk sample is likely under significant compressive stress. However, it must also be noted that the quantitation and interpretation of frequency shifts of Raman bands in glasses are challenging problems. For example, change in glass composition during ion-exchange may alter the Raman scattering cross sections of the high-frequency stretching modes of various Q-species. In addition, frequency shifts of these bands may not be simply related to changes in bond lengths and/or angles as compositional modification accompanying ion-exchange may lead to changes in the anharmonicity and non-linear effects (mode coupling) which would also affect various mode frequencies.

4.3. Effect of the modifier cation field strength on the Na^+/K^+ interdiffusion properties

As shown in Fig. 1, the K^+ penetration depth for the SNM glass containing MgO is significantly higher than the SNC glass containing CaO. On the other hand, the ^{23}Na δ_{iso} values for the SNM and SNC glasses containing similar $Na/(Na + K)$ ratios (Fig. 3) indicate that the Na–O interatomic distance is higher in the glasses containing Mg^{2+} compared to their counterparts with Ca^{2+} . This difference is likely related to the higher field strength of Mg^{2+} ($FS = 0.46$) in comparison with Ca^{2+} ($FS = 0.36$). Hence, in SNM glass, the Mg will primarily interact with the NBO and the Na^+ will be mostly associated with BO, forming longer and weaker bonds compared to Na–NBO [22]. These weaker Na–BO bonds would facilitate the Na^+/K^+ interdiffusion coefficients in the SNM glass in comparison with that in the SNC glass, as is indeed manifested in the corresponding K^+ penetration depths for these glasses (Fig. 1).

5. Summary

Stress/structural relaxation in silicate glasses during Na^+/K^+ ion-exchange controls the level of the developed compressive stress and

hence, the mechanical response of the material. Therefore, an atomistic understanding of the stress relaxation mechanisms in these glasses is essential to optimize the ion exchange process. The ^{23}Na and ^{29}Si NMR spectroscopic results reported in the present study demonstrate that significant structural adjustments are induced by Na^+/K^+ ion exchange in binary and ternary silicate glasses. These structural adjustments include (i) a shortening of the average Na–O and Si–NBO distances and (ii) an opening/increase of the Q^4 Si–O–Si bond angle, both of which relieve the stress by better accommodating the larger K^+ in the glass structure. Similar structural modifications are also observed when Na is replaced by K in analogous glasses derived via the melt-quench route. In contrast, in this study, no significant change in the Q^n species distribution is observed as a result of the ion exchange. These results are consistent with the concept of “Fast delayed-elastic relaxation” proposed by Varshneya et al. [2]. Finally, the effect of alkaline-earth ion on the K^+ penetration depth in Na,Ca and Na,Mg-silicate glasses is investigated. This penetration depth is longer in Na-silicate glasses containing MgO compared to that in analogous glasses containing CaO. This difference is attributed to the higher field strength of Mg^{2+} compared that of Ca^{2+} that results in strong interaction of Mg^{2+} with the NBO atoms and hence, the Na–O bonding ion Na,Mg-silicate glasses predominantly involve bridging oxygen atoms [22]. This bonding scenario gives rise to readily exchangeable Na^+ in larger Na–O cages and consequently increasing K^+ penetration depth in Na,Mg-silicate glasses, compared to that in their Na,Ca analogues.

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