



Vibrational study of thermally ion-exchanged sodium aluminoborosilicate glasses



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ABSTRACT

Thermally ion-exchanged M⁺-for-Na⁺ (M = K and Ag) aluminoborosilicate glasses were obtained from the glass (SiO₂)₆₀(B₂O₃)₁₀(Al₂O₃)₆(Na₂O)_{20.2}(ZrO₂)_{3.7}(Sb₂O₃)_{0.1} (in mol%) and studied by infrared reflectance and micro-Raman spectroscopy. The results of both techniques are consistent with local structural rearrangements induced by ion-exchange below glass transition temperature, T_g , and are expressed for the silicate network by the chemical equilibrium $Q^2 + Q^4 \rightleftharpoons 2Q^3$ where Q^n represents a silicate tetrahedron with n bridging oxygen atoms. Replacement of Na⁺ by K⁺ was found to shift this equilibrium to the right, while the introduction of Ag⁺ ions causes the opposite effect. Micro-Raman depth profiling showed that these structural changes occur within a layer whose thickness depends on the type of the guest cation and the conditions of ion-exchange; the thickness is about 50 μm for Ag⁺ ions exchanged at 340 °C for 180 min and about 40 μm for K⁺ exchanged at 325 °C for 6 h.

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1. Introduction

Ion-exchange below glass transition temperature is a well known technique to modify the mechanical [1–3] and optical [4–6] properties of glasses. Typically, a sodium silicate glass is submerged in a bath containing a molten salt (e.g. KNO₃) at elevated temperatures. Due to differences in chemical potential, Na⁺ cations from the glass will migrate to the molten salt bath while an equal number of guest cations from the molten salt will replace the migrating Na⁺ ions. When the guest cations are larger than sodium, for instance when K⁺ is substituted for Na⁺, this replacement causes the glass surface to be in a state of compression [1–3] (chemical pressure) that may reach several hundreds of MPa, thus leading to the chemical strengthening of glass. The optical properties of glass are also altered when Na⁺ ions are substituted by more polarisable (e.g. Ag⁺) ions. Such a local modification of the refractive index can be used for developing waveguides, micro-optics, etc.

Despite the technical applications of ion-exchange there are still open questions concerning its mechanism at the molecular level, including the possibility for structural changes induced by ion-exchange below T_g . Such changes would allow for the accommodation of guest cations in a network suited initially for the host cations and would manifest the ability of glass to modify its local structure even below T_g , where the network structure is generally considered to be unaffected by ion-exchange (see, for example, Ref [5]).

In order to address these issues, we have carried out a combined infrared reflectance and micro-Raman spectroscopy study on two glasses derived from the glass (in mol%) (SiO₂)₆₀(B₂O₃)₁₀(Al₂O₃)₆(Na₂O)_{20.2}(ZrO₂)_{3.7}(Sb₂O₃)_{0.1} (Na-glass hereafter) by thermally ion-exchanging K⁺-for-Na⁺ (K-glass) and Ag⁺-for-Na⁺ (Ag-glass). The aim of this work is to search for correlations between the type/penetration depth of the guest cations and possible structural changes induced by ion-exchange. The spectroscopic results show unambiguously that ion-exchange induces local changes in glass structure; they are manifested mainly by rearrangements in the silicate tetrahedral units Q^n even at temperatures below T_g and depend directly on the nature of the guest cations which replace the sodium host cations in the Na-glass.

2. Experimental

2.1. Sample preparation

The Na⁺-glass was synthesized at 1560 °C by melting an appropriate 150-g batch in silica crucible for 2 h, including 90-min of melt stirring. The starting reagents were chemically pure SiO₂, Al₂O₃, H₃BO₃, Na₂CO₃, ZrO₂ and Sb₂O₃. ZrO₂ and Sb₂O₃ were added in order to improve glass stability in molten salts and to avoid microbubbles, respectively. The melt was quenched by pouring out into a brass mould, and the resultant glass was annealed for 2 h at glass transition temperature $T_g = 555$ °C which was determined using viscosity measurements. Na-glass samples were exposed to a melt of dilute AgNO₃ (95 mol% NaNO₃ and 5 mol% AgNO₃) at 340 °C for 180 min. This procedure was expected [4] to result in almost full replacement of Na⁺ ions in the subsurface

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regions by Ag^+ ions from the melt. K^+ ion-exchange was performed in a bath of pure KNO_3 melt at 350°C for 6 h. Both samples remained optically transparent after ion-exchange.

2.2. Vibrational spectroscopy

All spectroscopic measurements were performed at room temperature on polished plane-parallel sample plates of 1.5 mm in thickness. The infrared (IR) spectra were measured with a vacuum spectrometer at the specular reflectance mode (11° of normal) with 2 cm^{-1} resolution. The IR reflectance spectra were analyzed by Kramers–Kronig transformation to yield the absorption coefficient spectra, $a(\nu)$, from the expression $a(\nu) = 4\pi\nu k(\nu)$ where $k(\nu)$ is the imaginary part of the complex refractive index and ν is the infrared frequency in cm^{-1} . After the IR measurements, the ion-exchanged glass samples were cut and micro-Raman spectra were acquired from their cross-section to probe structural evolution as a function of depth from the edge of the glass surface. Raman measurements were performed with a dispersive confocal microscope at back scattering geometry, with 488 nm excitation, 2 cm^{-1} resolution and spatial resolution better than $1\ \mu\text{m}$.

3. Results

3.1. IR spectroscopy

Fig. 1 shows that the far-IR spectra of the pristine Na-glass and of the two ion-exchanged glasses exhibit broad peaks characteristic of Na^+ -site (ca. 210 cm^{-1}), K^+ -site (170 cm^{-1}) and Ag^+ -site (122 cm^{-1}) vibration modes. This result is in very good agreement with the simple harmonic oscillator model considering only the cation-mass effect (inset of Fig. 1), and also with previous findings for alkali- and silver-containing borate and silicate glasses [7–9]. Thus, far-IR spectroscopy provides direct evidence for the replacement of Na^+ by K^+ and Ag^+ by ion-exchange at least in the depth probed by the far-IR beam (ca. $10\ \mu\text{m}$).

Introduction of different guest cations in the glass matrix does not create new bands in the mid-IR range. However, ion-exchange affects the bandwidth of the main IR feature at ca. 850 to 1250 cm^{-1} (Fig. 2), where the infrared activity results from the convolution of Si–O stretching modes of different Q^n silicate species (see Ref [9] and references therein). Fig. 2 shows that replacement of Na^+ by K^+ leads to narrowing, while Ag^+ -for- Na^+ exchange causes broadening of the 850 – 1250 cm^{-1} spectral envelope. These results are in excellent agreement with previous findings for ion-exchanged soda-lime silica

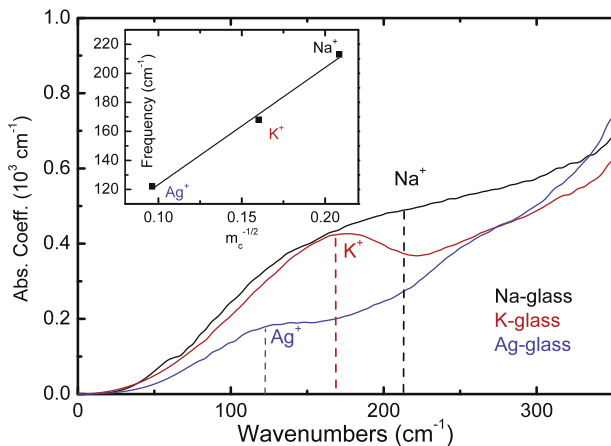


Fig. 1. Far-IR spectra showing peaks due to cation-site vibrations for the Na-glass and for the K^+ -for- Na^+ and Ag^+ -for- Na^+ ion-exchanged. In the inset m_c (in au) is the cation mass.

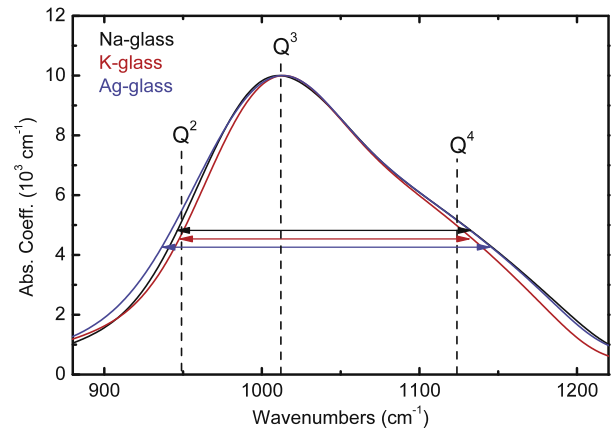


Fig. 2. Expanded view of the 850 – 1250 cm^{-1} IR range due to Si–O stretching vibrations of different Q^n silicate units as indicated by vertical lines. Replacement of Na ions by K and Ag ions by ion-exchange causes narrowing and broadening, respectively, of this spectral range.

(float) glasses [9,10] and are consistent with the following chemical equilibrium



Fig. 2 suggests that equilibrium (1) shifts to the right for K^+ -for- Na^+ and to the left for the case of Ag^+ -for- Na^+ ion-exchange.

3.2. Raman spectroscopy

Micro-Raman spectra measured at various depths from the surface of the K^+ -for- Na^+ ion-exchanged glass are shown in Fig. 3 in comparison with that of the pristine Na-glass. The following trends are observed as a function of distance from glass surface: (i) the intensity of the peak

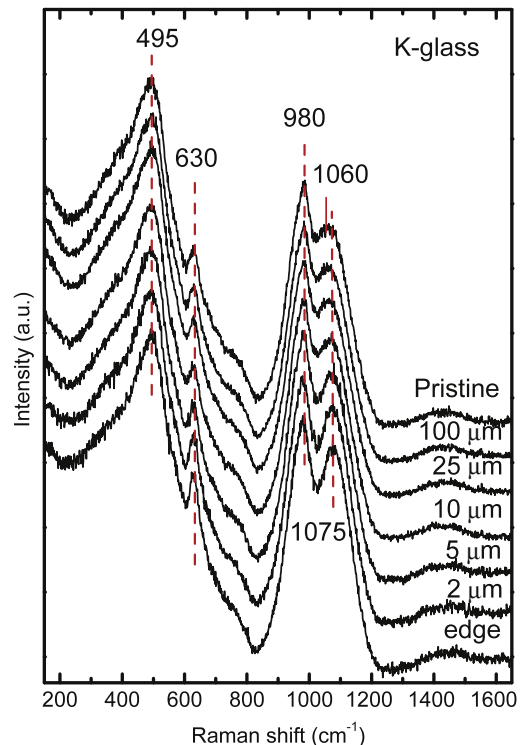


Fig. 3. Micro-Raman spectra of the K^+ -for- Na^+ ion-exchanged glass measured at different depths from the glass surface in comparison with the spectrum of the pristine Na-glass.

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