Journal of Non-Crystalline Solids xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

A XANES investigation of the network-modifier cations environment before and after the Na^+/K^+ ion-exchange in silicate glasses

C. Ragoen[a,*], L. Cormier[b], A.-I. Bidegaray[a], S. Vives[a], F. Henneman[c], N. Trcera[d], S. Godet[a]

[a] Université Libre de Bruxelles, 4MAT Department, CP165/63, Avenue F. Roosevelt 50, B-1050 Brussels, Belgium
[b] Institut de minéralogie, de physique des matériaux et de cosmochimie (IMPMC), Sorbonne Universités, UPMC Univ Paris 06, CNRS UMR 7590, Muséum national d'Histoire naturelle, IRD UMR 206, 4 place Jussieu, F-75005 Paris, France
[c] AGC Glass Europe, Technovation Centre, Rue Louis Blériot 12, B-6041 Gosselies, Belgium
[d] Synchrotron SOLEIL, L'Orme des Merisiers 48, St Aubin, 91192 Gif-sur-Yvette Cedex, France

ARTICLE INFO

Keywords:
Glass
Ion-exchange
Stress relaxation
XANES

ABSTRACT

μ-XANES is used to study the modifications in the alkali and alkaline-earth environments induced by the Na^+/K^+ ion-exchange process in various Na –silicate glasses. The results indicate that the ion-exchange process induces a shortening of the Na—O, Ca—O and Mg—O bond distances. The contraction of the Na—O, Ca—O and Mg—O coordination shell allows a better accommodation of the K^+ cations in the glass network and thereby leads to partial relaxation of the stress developed by the Na^+/K^+ ion-exchange. Nevertheless, despite the stress relaxation process, the K^+ environment in the ion-exchanged glass is not equivalent to the one in Na,K–silicate as-melted glasses. Hence, this study clearly shows that the ion swapping forced K^+ cations to occupy smaller sites which are not achievable via the melt quench route for glasses with the same K amount.

1. Introduction

The chemical strengthening via ion exchange is a well-known industrial process consisting in replacing smaller Na^+ cations near the surface by larger K^+, in a molten salt bath at a temperature below the glass transition temperature (T_g) [1]. This process results in the formation of an ion-exchanged region near the glass surface that is under significant compressive stress. While the chemical strengthening process was discovered in the early 1960′s, the structural modifications induced by Na^+/K^+ ion exchange in silicate glass are still poorly understood. In particular, the question remains as to how the K^+ cations are accommodated by the Na^+-host modifier cation and other divalent cations in the glass.

Previous studies on structural modification induced by the ion exchange process were carried out using molecular dynamic (MD) simulations [2–4], nuclear magnetic resonance (NMR) spectroscopy [5] and micro-Raman spectroscopy [6,7]. These MD studies mainly focus on the silicate network adaptation mechanisms following the Na^+/K^+ ion exchange and on the difference in potassium-oxygen coordination number (CN) between the ion-exchanged and the compositionally-equivalent potassium as-melted glass. In the NMR study, the atomistic details of the structural adaptation of the Na^+-host modifier cation and the Si—O network were analyzed [5]. Hence, no attention has been paid to the environments of network-modifiers divalent cations before and after the ion-exchange process.

The X-ray Absorption Spectroscopy (XAS) technique is a powerful method to study the environment around one specific element in a disordered multicomponent material [8]. Moreover, the use of μ-XANES (X-ray Absorption Near Edge Structure) technique allows following the local environment of desired element at different locations within the diffusion area. Indeed, XANES is highly sensitive to the symmetry and the medium range order around the absorbing atom [9]. However, due to the multiple scattering effects, the interpretation of the XANES spectra is difficult and a comparison with spectra of crystalline references compounds is necessary [9].

Here, we report the results of μ-XANES measurements on Na^+, K^+, Ca^{2+} and Mg^{2+} ions at different location within the interdiffusion area in Na^+/K^+ ion-exchanged binary Na –silicate and ternary Na,Mg and Na,Ca–silicate glasses. These results were compared with those obtained from Na,K–silicates as-melted glasses compositions.

2. Experimental methods

2.1. Glass synthesis

The glass compositions investigated in this study are shown in

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[*] Corresponding author.
E-mail address: ceragoen@ulb.ac.be (C. Ragoen).

http://dx.doi.org/10.1016/j.jnoncrysol.2017.10.021
Received 13 July 2017; Received in revised form 22 September 2017; Accepted 12 October 2017
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Please cite this article as: Ragoen, C., Journal of Non-Crystalline Solids (2017), http://dx.doi.org/10.1016/j.jnoncrysol.2017.10.021

Table 1
Analyzed chemical compositions (in mol%) of all the glasses investigated in this study.

Sample	SiO_2	Na_2O	K_2O	CaO	MgO
SN	78 ± 2	22 ± 2	0	0	0
SNC	64 ± 4	25 ± 4	0	11 ± 1	0
SNM	64 ± 1	27 ± 1	0	0	9 ± 1
SN19K	71 ± 1	10 ± 2	19 ± 2	0	0
SN14K	72 ± 2	14 ± 3	14 ± 3	0	0

Table 2
Run condition for XANES measurement.

K-Edge	Energy range (eV)	Step (edge region)	Counting time per point (s)	Monochromator
Na	1040–1150	0.2	6	Multilayer grating
Mg	1280–1400	0.2	2	Multilayer grating
K	3520–3800	0.2	2	Si (111) crystal
Ca	3980–4250	0.2	2	Si (111) crystal

Table 1. These glasses were synthesized from constituent oxide and carbonate precursors. The constituents were melted in a platinum/rhodium crucible for 2 h between 1400 °C and 1500 °C depending on the composition. The melt was then quenched and the resulting glass was crushed and remixed followed by remelting for two additional hours to improve glass homogeneity. The final melts were finally quenched on a graphite plate and annealed for 12 h at the respective glass transition temperatures (Tg), in order to release the internal stresses. The resulted glass compositions were analyzed by X-ray fluorescence (XRF, Siemens Bruker S4 PIONEER, Cu Kα radiation) and are listed in Table 1, with the notation SN(C,M) where S is for silicon, N for sodium, C for calcium and M for magnesium. Note that the SN19K and SN14K glasses were produced in order to compare the environment of Na and K in Na^+/K^+ ion-exchanged SN glasses with Na,K–silicates as-melted glasses compositions.

2.2. Ion-exchange and related measurements

2.2.1. Ion-exchange process

The SN, SNM and SNC glassy samples with dimensions 4 cm × 4 cm × 4.1 mm were polished, placed in a stainless steel rack and they were then immersed in a molten salt bath containing 50 kg of KNO_3 at 400 °C. In order to have similar diffusion depths and such as in [5], the SN glass was immersed for 24 h and the SNC and SNM remained 66 h in the bath. At the end of the ion-exchange process, the samples were removed from the bath and cooled to room temperature and then washed in water. In what follows the xx number after the glass name corresponds to the depth of exchange in the material with 00 corresponding to the glass surface. For example, SNM00 represents the surface of the SiO_2-Na_2O-MgO glass and SNM168 is the location at 168 µm in the depth of the material.

2.2.2. Interdiffusion characterization

The ion-exchanged 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 (atom%) were determined using Energy Dispersive X-ray spectroscopy in a scanning electron microscope (FEG-SEM, Hitachi SU 70). The K profiles were obtained by performing line scans from the surface to a desired depth in the material. The measurements were performed with an accelerating voltage of 15 kV and a dwell time of 1 s, using 1 cm^2 solid-state detector.

2.3. XAS measurements

Na, K, Ca and Mg K-edges µ-XANES spectra were collected on LUCIA beamline at the SOLEIL synchrotron (Saint-Aubin, France), with an injected electron energy and current of 2.75 GeV and 450 mA, respectively. All the spectra were recorded in fluorescence mode with a silicon drift diode detector. Two KB mirrors were used to focus the beam down to 5 × 5 µm and then profiles were realized on cross-section of the ion-exchanged glasses. µ-XRF profiles from the surface to the interior of the glass were realized on every ion-exchanged glass samples used for the interdiffusion characterization in order to position precisely the surface of the glasses and to choose the most adequate positions to record XANES spectra subsequently. The run conditions are reported in Table 2. Crystalline references were uniformly deposited as powders on a graphite tape.

The normalization procedures and the self-absorption corrections were realized on all the spectra with the same parameters using the Athena software [10].

3. Results

3.1. Interdiffusion behavior

In Fig. 1, the potassium profiles for the SN, SNM and SNC glasses are represented. The depth of interdiffusion ranges between 100 and 160 µm.

3.2. Na environment

The Na K-edge spectra of ion-exchanged SN, SNM and SNC glasses at the surface and deeper in the glasses are shown in.

Fig. 2 and compared to the as-melted SN19K and SN14K glasses. The spectra are composed of three features. The first peak, denoted A, corresponds to a pre-edge transition of the Na K-edge. For all the glass composition, this pre-edge appears around 1069 eV. No clear displacement of this peak or any change in its intensity can be observed for the different glasses compositions and treatments. The edge crest corresponds to a doublet and the same absence of displacement is observed for the B peak that is located at 1072 eV. In contrast, a small displacement of the C peak of the SNM and SN glasses to higher energy is observed at the surface in comparison with the end of the interdiffusion depth. Note that the relative intensities of peaks B and C are the same for all the glasses and nearly equal to one. The Na K-edge XANES spectra for the ion-exchanged glasses are noisier at the surface due to the lower Na concentration.

In Fig. 3, the Na K-edge spectra of the as-melted SN14K is compared to three crystalline references: albite ($NaAlSi_3O_8$), jadeite ($NaAlSi_2O_6$) and nepheline ($Na_3KAl_4Si_4O_{16}$). The spectra for the crystals are similar

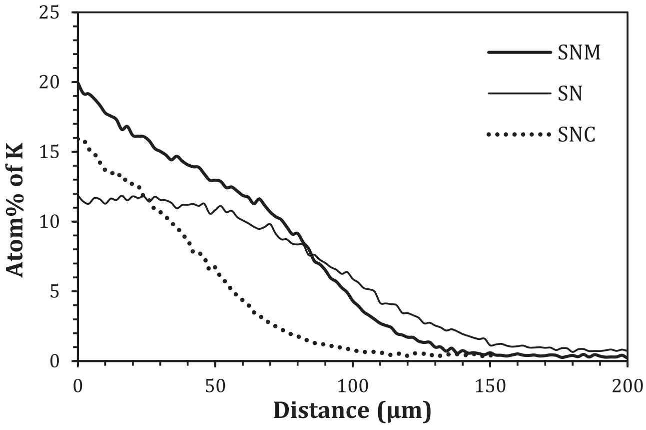

Fig. 1. K concentration as a function of the depth in the material for the SN, SNM and SNC glasses.

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