



# Analysis of the surface structure of soda lime silicate glass after chemical strengthening in different $\text{KNO}_3$ salt baths



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## ABSTRACT

This paper deals with the physico-chemical and mechanical properties of soda lime silicate float glass treated in  $\text{KNO}_3$  baths with different purity levels. The potassium concentration profile in the surface layers was measured by EDXS and correlated with the residual stress frozen in the material, which was determined by a procedure based on the measurement of the strengthened sample curvature deriving from progressively etching one of its surfaces. This allowed pointing out a significant influence of the used salt. In order to better understand the phenomena and mechanisms underlying the surface equilibrium conditions, micro-Raman measurements were also performed on the glass surface in the aim to investigate the variation of the glass microstructure after ion-exchange in the different salt baths.

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## 1. Introduction

Ion exchange in glass is now a hundred years old technique. In fact, although ion exchange occurrence can be detected in some processes used for the creation of “luster” decoration on Medieval and Renaissance pottery [1–4], modern ion exchange techniques used to modify the surface properties of glass date back to 1913 when Schulze [5] demonstrated that monovalent cations contained in glass can be exchanged when a soda lime silicate glass is immersed in a bath of molten silver nitrate. In time, ion-exchange processes were developed and industrialized for many applications, such as chemical strengthening of glass articles [6,7], gradient index (GRIN) lenses [8,9] and planar waveguides [10]; the ion exchange properties of glass have also been used to explain operation of the pH glass electrode and the chemical durability of glass [11].

In recent years, ion exchange has acquired renewed interest as an effective strengthening technique for silicate glasses. The exchange of small ions such as  $\text{Li}^+$  or  $\text{Na}^+$  in an alkali-containing glass, with larger ions such as  $\text{K}^+$  from a molten  $\text{KNO}_3$  bath at temperatures below the strain point of the glass, is responsible for the creation of bi-axial residual compressive stress in the surface layers of the material. Because glass products generally break due to excessive tension applied at a surface flaw, the introduction of surface compression strengthens the glassware. This process, called “ion exchange strengthening” or “chemical strengthening”, was originally described by Kistler [12] and Acloque and Tochon [13] in 1962 showing how the interdiffusion of ions can increase the strength of glass by 3–4 times. Irrespective of the

expensiveness of the process, several chemically strengthened glass products have been successfully marketed, such as aircraft cockpit windshields, transparent armor, glass substrates for harvesting solar energy, high strength-to-weight ratio glass containers, auto-injector cartridges, photocopier glass, computer disks, and thin display windows in electronic communication devices (monitors, cell phones, tablets and MP3 players) [14]. The main advantages of chemical strengthening compared with the more wide-spread thermal tempering process [15] are both the higher surface stress, and the possibility of application to shaped articles (curved or hollow), also with a low thickness, thus avoiding many of the problems associated with thermal tempering such as optical distortion of the surface and premature failure due to NiS inclusions. For instance, in the case of soda-lime-silicate float glass, thermal tempering allows to increase the bending strength of about 100–200 MPa with respect to the annealed material, while ion-exchange can allow increases of more than 400 MPa [15,16].

Typically, an industrial ion exchange process is performed by placing the glass components for several hours (from 4 to even 120 h) in a vessel containing a molten salt; in the most typical configuration sodium (or lithium) containing silicate glass is immersed in molten potassium nitrate at temperatures below the strain point [16–18]. During the process, glass cations ( $\text{Na}^+$  or  $\text{Li}^+$ ) exchange with the salt ions, which migrate into the glass network by the inter-diffusion mechanism described with Nernst-Planck equations. The final strengthening is a function of the type of invading ion (salt bath composition), and of both the bath temperature and the immersion time.

In the past, apparently little attention has been paid to the role of the salt composition on the chemical, physical and mechanical properties of the treated glass. Some recent results [19] indicated a more effective ion-exchange process when the glass article is immersed in a bath containing significant amount of the ion in the glass to be exchanged.

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So, a renewed interest in the analysis and understanding of the influence of salt bath composition on the ion-exchange process and on the consequent properties of silicate glasses has been grown.

In this work commercial soda lime silicate float glass underwent ion exchange in nominally pure  $\text{KNO}_3$  salts, of different provenance. The treated samples were characterized in terms of both potassium penetration profile and mechanical strength, in order to define the influence of the bath composition on the final performances. Moreover, micro-Raman spectroscopy measurements were carried out from the glass slab beneath the surface in the aim to investigate the microstructure of the silica network of the different samples.

## 2. Experimental

Soda lime silicate float glass, from a single original commercial sheet 4 mm thick which was cut in  $50 \times 50$  mm slides, was used in this work. The weight composition of the glass is 71%  $\text{SiO}_2$ , 13%  $\text{Na}_2\text{O}$ , 1%  $\text{K}_2\text{O}$ , 9%  $\text{CaO}$ , 4%  $\text{MgO}$ , 1%  $\text{Al}_2\text{O}_3$ , and 1% trace elements. The glass transition temperature measured by the Differential Scanning Calorimeter (DSC) (DSC2010, TA Instruments, USA) method [20] was 577 °C.

The samples were subjected to ion exchange treatment in a small semi-automatic furnace allowing treatment of 19 samples at the same time. Four different potassium nitrate salts were used: a Sigma Aldrich analytical grade with nominal purity >99.0%, a salt from Haifa-Eurochemicals with nominal purity >99.4%, a salt from an unknown source that had been already used for at least 1000 h in  $\text{Na}^+ - \text{K}^+$  ion-exchange treatments and a salt from Lema with nominal purity >99.0%; the used salt was labeled as C; the other three were randomly labeled as A, B and D.

The salts were subjected to chemical analysis before and after the ion exchange process via dissolution in 2 vol.%  $\text{HNO}_3$  water solution that was analyzed by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) (Spectro-Ciros, Germany); a multi-element standard (sol.IV, Merck) was used for the titration of the dissolved ions with the exception of  $\text{Na}^+$  and  $\text{K}^+$ ; for the determination of these elements, specific standards were prepared dissolving variable amounts of ultrapure  $\text{KNO}_3$  (99.999%) and  $\text{NaNO}_3$  (99.995%) (Sigma-Aldrich) in bi-distilled water.

The following conditions were used for every sample: pre-heating within the furnace just above the salt bath surface (20 min), ion exchange process at 450 °C (4 h or 24 h), and post-cooling above the salt bath surface (20 min).

The mechanical characterization was carried out by measuring the bi-axial flexural strength [21,22] using a ring-on-ring configuration (loading ring and lower support ring having diameters of 20 mm and 40 mm, respectively) with an actuator speed of 1 mm/min configuration. The tests were performed also on one set of as-cut glass specimens, for comparison.

The surface compression stress was measured by means of a standard optical method based on the photoelastic properties of the glass with a surface stress meter Luceo FSM-60LE. The results are given with 20 MPa uncertainty [23].

Fragments of the samples collected after mechanical testing were used to measure the potassium penetration profile in the surface layers. The specimens coated with Au-Pd alloy by sputtering were placed within a Scanning Electron Microscope (SEM) (JSM5500, Jeol, Japan) and clean flat portions of the fracture surface were analyzed and the potassium  $\text{K}\alpha$  signal was recorded on specific paths (about 40  $\mu\text{m}$  long) using the Energy Dispersion X-ray Spectroscopy (EDXS) (EDS2000, IXRF System, USA) probe. A similar procedure was used to determine the chemical composition of the external surface of the glass samples, before and after the ion exchange process. The analysis was carried out on at least 5 different samples for each ion exchange condition. Standardless quantitative EDXS analysis was performed using EDS2000 software within the IXRF System, with the ZAF (Z—atomic number, A—X-ray absorption, F—X-ray fluorescence) matrix-correction method.

The  $\text{Na-K}\alpha$ ,  $\text{K-K}\alpha$ ,  $\text{Si-K}\alpha$ ,  $\text{Al-K}\alpha$ ,  $\text{Mg-K}\alpha$ ,  $\text{Ca-K}\alpha$  and  $\text{O-K}\alpha$  spectral lines were used for the analysis. The base glass was used as reference to improve the accuracy of the quantitative analysis.

Micro-Raman spectra were taken at room temperature in parallel-polarization mode and in backscattering geometry using a triple-axis monochromator (Horiba-Jobin Yvon, model T64000), set in double-subtractive/single configuration, and equipped with three holographic gratings of 1800 lines/mm. The spectra were excited by the 514.5 nm line of a mixed Ar-Kr ion gas laser. The laser beam was focused onto the cross section of a cut sample, near the surface region, with a spot of about 1  $\mu\text{m}$  in size, and the scattered radiation from this region was collected in confocal mode exploiting the same objective used to focus the incident laser beam. An 80 $\times$  microscope objective (N.A. = 0.75) was used to excite and collect the Raman spectra.

## 3. Results

The concentration profiles of the glass treated with salt A, for exchange times of 4 and 24 h, are shown in Fig. 1. For all types of salts, the concentration profiles  $C(x,t)$  can be fitted with the function:

$$C(x,t) = C_0 \operatorname{erfc}\left(\frac{x}{\sqrt{2Dt}}\right) \quad (1)$$

where  $C_0$  is the surface concentration,  $x$  is the depth,  $t$  the treatment time and  $D$  the inter-diffusion coefficient. This is the analytical solution for a concentration profile obtained from a source at constant concentration  $C_0$ , where the diffusion coefficient is assumed to be constant. The function  $\operatorname{erfc}$  is the complementary error function [24]:

$$\operatorname{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty \exp(-y^2) dy. \quad (2)$$

The thickness of exchanged region, here defined as the depth for which  $C/C_0 = 0.02$ , is independent of the salt bath used for the ion-exchange process and it is equal to  $\approx 14 \mu\text{m}$  and  $\approx 31 \mu\text{m}$  for process times of 4 h and 24 h, respectively. The inter-diffusion coefficient is assumed also independent of the ion-exchange duration and the used  $\text{KNO}_3$  melt, being always equal to  $1.2 \div 1.1 \times 10^{-11} \text{ cm}^2/\text{s}$ . This value is again in fair agreement with previously published results obtained on soda-lime silicate glass by Shen et al. [25] and Jiang et al. [26] using similar ion exchange conditions. In fact, in these works the inter-diffusion coefficient was shown to be slightly concentration dependent [25–27]: for example, Shen et al. estimated that the potassium diffusion coefficient in soda-alumina-silicate glass at 450 °C increases of about

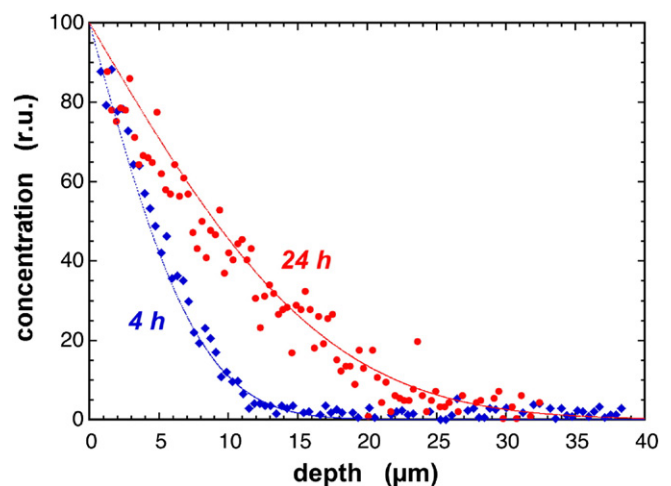


Fig. 1. Potassium concentration profile after 4 h and 24 h of treatment in salt A.

10% when K<sub>2</sub>O load in the glass changes from 3 wt.% to 12 wt.% [25]; more recently, Jiang et al. obtained similar results on soda-lime-silicate glass [26]. Nevertheless, the inter-diffusion coefficient is here considered as constant, without losing significance, in order to simplify the calculation procedure [7,25].

The main difference between the glass slides treated in the different salt baths is the surface concentration of potassium, which strongly depends on the used bath.

In Table 1 we report the percentage of exchanged sodium in the glass after ion exchange processes of 4 and 24 h, respectively. In addition, the amount of sodium in ppm and the detected impurities, as measured before and after ion exchange of 24 h, are reported there. For all the elements, for which no concentration value is quoted, the measured concentration was around or lower than 1 ppm.

As it can be observed, the ratio of exchanged sodium differs very much from a salt type to another and no apparent correlation can be noticed with the salt composition measured by ICP-OES. After the ion exchange in salt A, a considerable amount of sodium (about 80% of the initial content) still remains within the glass, only  $\approx 20$  mol% being replaced by potassium. The exchange efficiency is higher in bath B where  $\approx 55$  mol% of Na<sup>+</sup> is replaced by K<sup>+</sup> and it becomes very high in baths C and D where more than 70% of the sodium ( $\approx 85$  mol% in bath D after 24 h treatment) is replaced on the surface by potassium. In all the examined samples the substitution of Na<sup>+</sup> with K<sup>+</sup> is never complete and, moreover, the potassium surface concentration, cannot be directly related to the concentration of KNO<sub>3</sub> in the melt.

The results of the mechanical tests are summarized in Table 2, where are reported the sample mechanical strength in MPa, the surface compression stress in MPa and the specific surface compression, that is the surface compression divided for the molar concentration of exchanged potassium at the glass surface.

In general, the larger is the concentration of potassium after the ion exchange process, the higher are the strength and the stress. Therefore, the results in Table 1 can be directly correlated with those in Table 2, where the samples with the higher exchange ratio at the surface are characterized both by the higher mechanical strength and by the higher surface compression. The more interesting aspect is represented by the specific stress values: as can be observed, the salt giving rise to the lower surface concentration and stress actually gives the higher stress per potassium mole.

Fig. 2 shows the Raman spectra measured at the surface of the untreated glass and of the glass slides treated in the different salt baths.

In all of the spectra two regions can be identified: a lower frequency region, between 200 and 600 cm<sup>-1</sup>, characterized by the spectroscopic features related to the symmetric stretch vibration modes of oxygen in Si–O–Si linkages [28,29], and a higher frequency region, between 800 and 1200 cm<sup>-1</sup>, where a very complex spectral shape occurs because of peak convolution of the stretching vibration modes of oxygen [29,30]. In particular, the resulting broad feature is the convolution of peaks corresponding to symmetrical Si–O stretching vibrations in silicate tetrahedral SiO<sub>4</sub> units with different amounts of bridging oxygens (BO). These structural units are referred as Q<sup>i</sup> units where *i* stays

**Table 1**

First line: percentage of exchanged sodium, after 24 h, for every salt bath. Second and third lines: sodium concentration (ppm) and impurities for every salt bath. Fourth and fifth lines: sodium concentration (ppm) and impurities in every bath after 24 h of ion exchange.

	Salt A	Salt B	Salt C	Salt D
K <sup>+</sup> after 24 h	25%	50%	80%	85%
Na <sup>+</sup> before ie	10	97	2185	31
Imp. before ie	Zn, Ca, Mg	Cu, Zn, Ca, Mg	Cr (35), Zn, Ca, Mg, Sr, Co, Ni, Mo	Zn, Ca, Mg, Li
Na <sup>+</sup> after 24 h ie	159	733	3283	2732
Imp. after 24 h ie	Cr, Zn, Ca, Mg	Cr (10), Cu, Zn, Ca, Mg	Cr (40), Cu, Zn, Ca, Mg, Sr, Co, Ni, Mo	Cr (12), Cu, Zn, Ca, Mg, Li

**Table 2**

Mechanical strength, surface compression and specific surface compression for the samples treated in the different salt baths.

	Salt A	Salt B	Salt C	Salt D
Mech. strength (MPa)	294 ± 93	320 ± 173	614 ± 197	616 ± 186
Surface compression (MPa)	≈285	≈270	≈475	≈450
Specific surface compression (MPa/K <sup>+</sup> mole)	≈159	≈67	≈70	≈73

for the amount of BO in the tetrahedron, and the position of the corresponding peaks scatters appreciably, being reported at different wavenumbers in the literature reports. In fact, they were observed in the region between 1120–1190 cm<sup>-1</sup> (Q<sup>4</sup>) [31,32], 1100–1050 cm<sup>-1</sup> (Q<sup>3</sup>) [29], 1000–950 cm<sup>-1</sup> (Q<sup>2</sup>) [29], 960–900 cm<sup>-1</sup> (Q<sup>1</sup>) [29,33] and 850–800 cm<sup>-1</sup> (Q<sup>0</sup>) [29,34].

In the samples examined in this work, the high-frequency peak has its maximum at 1094 cm<sup>-1</sup>, which can be ascribed to the oxygen vibration frequency in Q<sup>3</sup> units. Two additional small features, at 954 cm<sup>-1</sup> and 995 cm<sup>-1</sup>, which can be associated to the oxygen stretching vibrations in Q<sup>1</sup> and Q<sup>2</sup> units, respectively, turn out as two shoulders of the main peak in the spectrum of the bare glass. The assignment of the small bump observed at 790 cm<sup>-1</sup> is a matter of debate: Colomban attributed this feature to the Q<sup>0</sup> unit [34], while MacMillan associated it to the Si vibration against its tetrahedral oxygen cage [29]. In our case the second hypothesis seems to be more plausible, since the low alkali concentration does not account for a high amount of Q<sup>0</sup> units as suggested from the peak intensity.

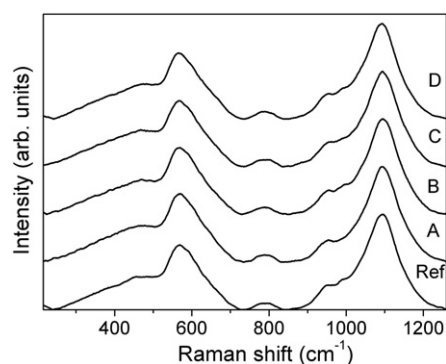
The spectra collected from the ion-exchanged samples are very similar, but a difference can be noticed in the region between 900 and 1050 cm<sup>-1</sup>, corresponding to the features related to Q<sup>2</sup> and Q<sup>1</sup> units, as evidenced in Fig. 3.

As it can be observed, in the ion exchanged samples the band component at 995 cm<sup>-1</sup>, corresponding to the Q<sup>2</sup> unit, is less evident in all the ion exchanged glasses and it completely disappears in the glass slides treated in salt A. This result is a characteristic of a rearrangement of the silicate structure with a lowering of the amount of non-bridging oxygens (NBO).

#### 4. Discussion

Generally the ion-exchange process of silicate glass alkali–alkali exchange is assumed to occur in a molar ratio of 1:1 although the exchange equilibrium at the glass surface is always less than 100% [35,36] especially when intense stress fields are involved due to a high difference between the ionic radii [37]. Some publications confirming this behavior are listed in Ref. [38].

Moreover, other papers report a measurable increase in ion-exchange efficiency and/or consequent reinforcing effect, when the



**Fig. 2.** Micro-Raman spectra measured at the surface of the reference glass and of the samples treated in the different salt baths.

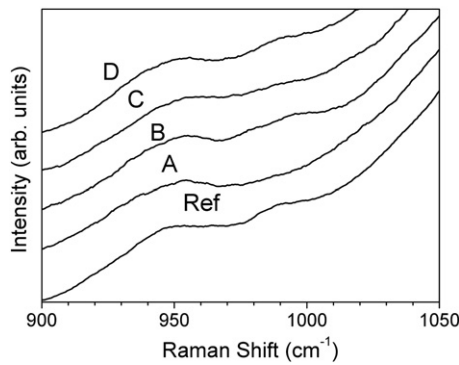


Fig. 3. Magnified plot of the Raman spectra in the region between 900 and 1050  $\text{cm}^{-1}$ .

process involves impure melted salts, although a clear explanation of the undergoing physical/chemical mechanism was not provided [19,39,40]. For example, Varshneya and Spinelli [19] performed chemical strengthening processes on high strain point lithium aluminosilicate glass in  $\text{NaNO}_3:\text{KNO}_3$  salt baths with molar ratios ranging from 5:95 to 50:50; they showed that the highest strength could be obtained by using 20 mol%  $\text{NaNO}_3$ .

Conversely, in other works, the presence of alkali or alkaline earth impurities is shown to be responsible for “poisoning” the melt or “blocking” the exchange [35,36,38,41,42]. Frischat in his famous book [38] summarized several experimental findings pointing out that the equilibrium between salt bath and glass can be influenced considerably by small amounts of the alkali ions in the bath (and, perhaps, also by other ions like  $\text{H}^+$ ). On the basis of the considered results, he concluded that a considerable amount of the alkali ions in the glass cannot be exchanged by other alkali ions in the melt, thus reducing the ion exchange efficiency to a large extent; this was due to micro-inhomogeneity and differential ion mobility in the glass [26]. Kolitsch and co-authors [35,36] analyzed the ion exchange process of  $\text{Na}_2\text{O}\cdot 0.35\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$  glass in  $\text{KNO}_3$  containing small amounts of alkaline earth ions and observed that Na–K exchange was “blocked” when Ba, Sr and, especially, Ca were present in the melt even in concentrations as low as 0.05 mol%; for concentrations of Ca in excess of 5 mol% the exchange is effectively canceled. Rauschenbach and Richter [41] proposed a thermodynamic model to explain how bivalent ions can inhibit the  $\text{Na}^+ - \text{K}^+$  exchange due to differing selectivity of the glass surface with respect to bivalent ions, which are exchanged in place of potassium, the effect occurring above a critical temperature called “blocking temperature”. More recently Zhang et al. [42] have shown that the  $\text{Na}^+ - \text{K}^+$  exchange in a soda-lime-silicate glass immersed in  $\text{KNO}_3$  can be reduced when Ca, Sr, Ba and Na ions are present in the melt bath; in this case too, calcium concentrations as low as 0.01 mol% were sufficient to limit the exchange and, therefore, affect the resulting strengthening.

Concerning this work, at present, it is hard to identify the elements or the mechanisms causing a so marked difference, both in composition and properties, between the samples treated in the different salt baths. A correlation with the sodium concentration is lacking, since the two most “efficient” baths are C and D, the former with 0.5 wt.% (0.4 mol%) of sodium and the latter with the lowest concentration of sodium. Moreover, the presence of Ca in the baths does not allow us to definitely explain the results obtained in this work since all the salts show very limited calcium concentration, always below 10 ppm, much lower than the 0.05 mol% (corresponding to about 200 ppm) necessary to inhibit the exchange on the basis of the results by previous authors [35,36,41,42] although the glass composition is not exactly the same.

A deeper inspection of the glass surface microstructure was performed by means of cross-sectional micro-Raman spectroscopy. This technique is a powerful tool but, nevertheless, it has to be outlined that the glass structure is a quite complicated system and at the present

state only empirical approaches can be developed in the aim to gain insights into the network microstructure. In the case of pure silica, the two main Raman bands have been extensively studied and they have been used for detailed analyses, based also on theoretical models, of the silica network in different treatment conditions [28,43,44]. On the other hand, for silicate glasses an accurate assignment for the low frequency region is still lacking, while a deeper investigation has been performed on the high frequency region, throughout the de-convolution of the Raman components due to oxygen stretching vibrations in the different tetrahedral units.

With regard to the lower frequency feature, the samples do not show any noticeable difference from the untreated glass. This band has been used in the analysis of indented glasses [45] where changes at  $700 \text{ cm}^{-1}$  were observed at stress fields higher than 6.5 GPa, which are values much higher than those measured in our samples.

As for the high frequency region the only observed change was the lowering and even the disappearing of the small feature related to the  $Q^2$  unit. In silica glasses these units have been with chain-like structures similar to crystalline metasilicates [30]. The lowering of the number of  $Q^2$  units must be followed by the increasing of the  $Q^3$  units, following a comproportionation reaction:



which keeps constant the NBO number [46]. The increase of  $Q^3$  units, related to sheet-like structures similar to crystalline disilicates [30], indicates the increase of the polymerization degree at the glass surface. In the spectra observed in this work, the amount of  $Q^2$  units is quite low so the change of their number does not affect the main  $Q^3$  peak within the sensitivity of the measurements.

Another empirical method used in literature for evaluating the polymerization degree of the glass network uses the ratio between the low-frequency and the high-frequency band areas [33]. In fact, in pure silica the high frequency peak has a very low intensity with respect to the lower frequency feature, since it is given by longitudinal and transversal optical (LO and TO) vibration modes which are Raman inactive [28–30]. The polymerization index has been used by Colomban and co-workers as a characterization index of glasses with different compositions [33,34] and in this work we use this index as a comparison parameter due to the indeterminateness in the quantitative evaluation of the amounts of  $Q^j$  units.

For the glass slides examined in this work, the polymerization index is 0.96 for the untreated glass, 1.10 for the sample exchanged in salt A, 1.03 for salt B, 1.06 for salt C and 1.00 for salt D, with an error bar of 0.02 evaluated by the uncertainty in selecting the spectra region for the intensity evaluation of the different spectral components. The above trend confirms that the  $\text{Na}^+ - \text{K}^+$  ion exchange induces the increase of the polymerization degree of the silica network. It is worth noting that the sample with the lower surface concentration of potassium (salt A) is characterized by the higher polymerization degree and by the higher specific stress value. This result indicates that the surface of the glass immersed in salt A developed a higher stiffness, which is probably at the origin of the quite low  $\text{Na}^+ - \text{K}^+$  exchange ratio.

Summarizing, besides the effects on the glass network induced by the incorporation of  $\text{K}^+$  ions, the salts can affect both the surface concentration and microstructure of glass in a remarkable way even with very low amounts of impurities. For instance, stiffer structures can be formed, which keep low the exchange ratio at the glass surface. At present it is not clear what are the salt properties or impurities playing the most relevant role in this phenomenon. Among the parameters not taken into account in this work, we can also consider the effect of anions, especially  $\text{OH}^-$ , on the exchange efficiency, as proposed in other previous works [47,48]. Therefore, it turns out evident that more fundamental thermodynamic study and experimental investigation will be required to clarify the remarkable effects due to small differences

in the melt salt composition on the ion-exchange process and on the correlated strengthening of soda-lime-silicate glass.

## 5. Conclusions

In this work, it has been established that small differences in the composition of the potassium nitrate salt bath have an important role in the strengthening process of soda lime silicate glass by ion exchange. The use of three commercially available  $\text{KNO}_3$  salts for industrial use and of a salt from an unknown source, which had been already used for at least 1000 h in different  $\text{Na}^+ - \text{K}^+$  ion-exchange treatments, resulted in very different strengthening effects that can be correlated with very different ion exchange efficiency. Micro-Raman analysis of the micro-structure of the glass surface pointed out an increase of the polymerization of the silica network in the sample where the lower exchange ratio was realized. This effect is coupled to a higher specific stress value which is indicative of a higher stiffness of the network.

At present, due to the relatively limited amount of contaminants in the salts used it is difficult to say whether the differences in strength and potassium concentration should be attributed to an increased ion-exchange efficiency in some melts or to effects determined for instance by the presence of alkaline earth ions in the melt as pointed out previously by Kolitsch et al. [35,36] or Zhang et al. [42]; more specifically, a clear behavior of the resulting strength or exchange efficiency cannot be defined as a function of sodium or other contaminants. Therefore, additional and more detailed analyses are required to specify the fundamental variables that influence the ion exchange process with the intent to design or choose optimal salt compositions. In particular, on the basis of these considerations, it seems necessary to verify the specific ion exchange efficiency and consequent strengthening effect of each particular salt with respect to the specific glass, before selecting the salt composition and using it for the ion exchange.

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