Ion exchange (IEX) in glasses is a well known technique to alter both mechanical (chemical strengthening) [1] and optical (refractive index) properties of silicate glasses [2]. Typically, a sodium silicate glass is submerged in a bath containing a salt (e.g. potassium nitrate) at elevated temperatures. This causes sodium cations in the glass surface to be replaced by other cations provided by the salt bath. When the exchanged cations are larger than sodium, for instance $K^+$ for $Na^+$, this replacement causes the surface of the glass to be in a state of compression [3]. This chemical pressure may reach several hundreds of MPa and thus enhances the glass hardness. Moreover, optical properties, such as refractive index, can be altered during the ion exchange process due to the exchange of sodium by a more polarisable cation such as $Ag^+$. This local modification of refractive index can be used for e.g. waveguides, micro-optics.

Although the ion-exchange process is well known, there are still open questions concerning the detailed mechanism in the atomic space scale. For instance, the possibility of ion-exchange induced changes on both, short and medium range order glass structure. The latter implies, that ion-exchange is not a simple procedure of cation replacement but also involves alteration of the glassy network to successfully accommodate the cations. Given that the ion-exchange process takes place far below the glass transition temperature $T_g$ [1-3], this will indicate that glasses are able to modify their structure even at temperature ranges where that they should act like a frozen supercooled liquid.

Recently [4], ion-exchanged $M^+$-for-$Na^+$ ($M = K$ and $Ag$) aluminoborosilicate glasses have been studied by infrared reflectance and micro-Raman spectroscopy. It was unambiguously shown that ion-exchange induces changes in the local order glass structure even at temperatures below $T_g$. For the silicate network, these structural changes can be quantified by micro-Raman depth-profiling spectroscopy and expressed by the chemical equilibrium $Q^2 + Q^4 \rightleftharpoons 2Q^3$ where $Q^n$ represents a silicate tetrahedron with $n$ bridging oxygen atoms. This equilibrium shifts to the left when $Na^+$ is replaced by $Ag^+$ and to the right when it is replaced by $K^+$ (see Fig. 1(b)). The 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. For $Ag^+$ ions, exchanged at 340 ºC for 180 min, the thickness is about 50 µm, whereas it is about 40 µm for $K^+$ exchanged at 325 ºC for 6 hours. It is discussed [4], that the local structural changes cannot be explained simply by the size difference effects between host and guest cations (surface pressure), but one has to consider also the acidic properties of the guest cations that drive to the establishment of suitable coordination environments. Thus, ion-exchange appears to be a cooperative process as it combines the diffusion of ions driven by chemical potential differences with local structural rearrangements, which are the response of the glass network to meet the needs of the guest cations for coordination environments suitable to their acidity [5].
On the other hand, the possibility of ion-exchange induced changes in the medium range order of the glass structure remains an open question. To address this issue and to confirm the micro-Raman spectroscopy observations with an independent method, we have performed a detailed nano-X-ray diffraction study at the PETRA III synchrotron of DESY research center. At beamline P03 we conducted XRD cross section depth profiling from the glass surface up to 100 μm into the bulk (see schematic Fig. 1(a)) of the same ion-exchanged aluminoborosilicate glasses previously characterized by micro-Raman spectroscopy [4]. The results of this study suggest that the medium range order, in a first approximation represented by the position of first sharp diffraction peak (FSDP) [6], is affected by the ion-exchange process resulting to a decrease of the relative spatial scales. The decrease of the d-spacing of the FSDP with increasing concentration of K⁺ and Ag⁺ cations (see Fig. 1(b)) is in agreement with the expected "compression" of the glassy network, given that pressure (static or chemical) mainly affects medium range order [6]. This implies that both medium and short range order of glasses are affected by the ion-exchange process. Moreover, the penetration depth of different ions, as determined by XRD measurements, is in excellent agreement with the previous spectroscopy studies. To give the full short- and midrange structural evolution upon cation replacement in the aluminoborosilicate glasses, the determination of the interatomic distances as a function of exchange depth is in progress.

References