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EXAFS Study of Silver and Rubidium Environments in Silicate Glasses

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Abstract. In order to study local order around Ag and Rb ions in ion-exchanged glasses EXAFS experiments were performed after thermal annealings at different temperatures below and above the glass transformation temperature. By means of Ag K-edge spectra three coordination spheres could be discussed. Whereas the two Ag-O distances remain unchanged during thermal treatments the Ag-Ag correlation exhibits the influence of the transformation of Ag ions to crystalline precipitations at elevated temperatures.

The Rb K-edge spectra present anomalous oscillations which can be ascribed to multi-electron excitations [1s3d]. In order to evaluate the main EXAFS signal, these features were subtracted using absorption data of gaseous rubidium. The Fourier transforms display similar Rb-O bond lengths within the first sphere for both the ion-exchanged soda-lime and the disilicate glasses while relaxation phenomena modify the second oxygen sphere towards the disilicate structure.

1. Introduction

The purpose of this work is to study the incorporation of single charged ions by an ion exchange process into silicate glasses replacing sodium. This is a useful technique generating refractive index profiles enabling the fabrication of passive waveguides for integrated optics devices and gradient-index lenses in glasses. Here, the incorporation of Ag and Rb ions has been investigated by EXAFS spectroscopy. These two ions were chosen because of their strongly different electron configurations (Ag: $4d^{10}$, Rb: $4p^6$) and ionic radii (Ag: 0.67 Å in twofold coord., Rb: 1.51 Å in sixfold coord.[1]). The first assumption to explain the behaviour of ion-exchanged glasses is a simple replacement of cations participating in the ion exchange process. However, short-range order experiments by X-ray absorption spectroscopy at the Ag K-edge showed structural rearrangements locally around silver as a result of a silver-sodium exchange well below the glass transformation temperature [2,3]. Therefore, the local order around Ag and Rb ions was investigated after an ion exchange or thermal annealing at different temperatures below and above the glass transformation temperature ($T_G = 535^\circ\text{C}$).

2. Experimentals

Commercial soda-lime glasses containing 13.8 mol% Na_2O , 72.0 mol% SiO_2 and 0.05 mol% Fe_2O_3 were ion exchanged in nitrate melts. The substitution of silver for sodium was carried out in $\text{AgNO}_3/\text{NaNO}_3$ melts at 330°C followed by thermal annealing at 380, 480 or 600°C . By comparison, the rubidium ions were incorporated into the glass network by means of pure RbNO_3 melts in the temperature range of 430 to 600°C in order to achieve a sufficient rubidium concentration.

The EXAFS measurements at the Ag (25.514 keV) and Rb (15.203 keV) K-edge were performed at the beam line RÖMO II of HASYLAB/Hamburg in transmission mode using a Si (111) or (311) crystal monochromator. The X-ray intensities were determined by ionisation chambers. The modified radial distribution functions of neighbours around the corresponding absorbing atom resulting from the Fourier transformed EXAFS oscillations were used to identify the different coordination spheres. The data were analysed using a curve fitting program of Ertel et al. [4] with the theoretical amplitude and phase functions calculated with FEFF 3 [5].

3. Results and Discussion

The Ag K-edge spectra were recorded up to > 27 keV that allows to identify three different spheres within the silver environment (Fig. 1). As it was to expect, the first two coordinations represent Ag-O correlations with a twofold oxygen coordination within the nearest neighbourhood of silver [2,6]. Thus the formation of a typical silver-like local order in contrary to the sodium environment can be confirmed. The third peak is mainly caused by Ag-Ag interactions. Whereas the first two peaks remain nearly constant during thermal treatments, only the intensity of the Ag-Ag correlations increases with increasing temperatures reflecting the influences of the transformation of silver ions to silver precipitations at elevated temperatures.

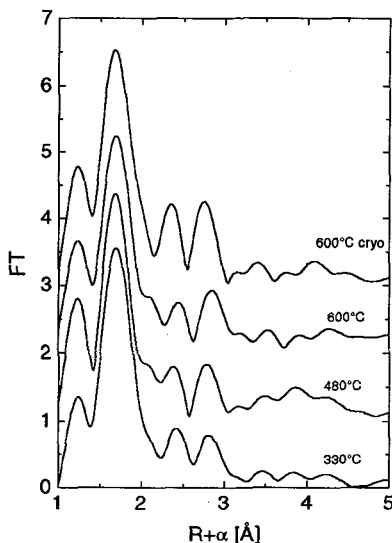


Figure 1: Fourier transforms of Ag K-edge spectra of the glass containing 1,7 mol% Ag_2O measured at room temperature and 77 K (cryo)

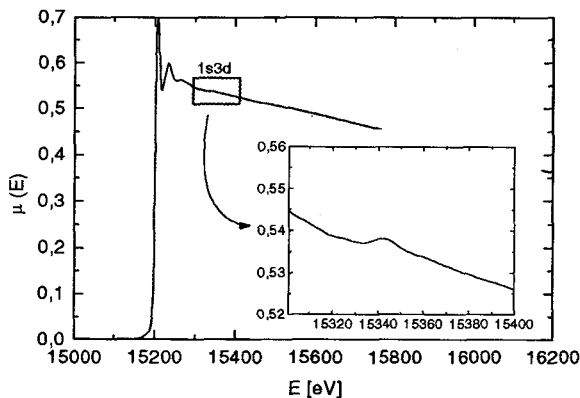


Figure 2: Rb K-edge EXAFS of a glass that was ion exchanged at 500°C

Because of the relatively low concentration of reducing iron ions this effect does not considerably change the spectra. The fitting procedures yield a Ag-Ag bond length at around 2.9 Å nearly independent on the thermal treatment. This distance is closely related to the fcc lattice parameter of crystalline silver.

The Rb K-edge spectra present anomalous oscillations which can be ascribed to multi-electron excitations of [1s3d] electrons (Fig. 2). In order to interpret the main EXAFS signal, these anomalies were subtracted by absorption of gaseous rubidium. The resulting Fourier transforms in Fig. 3 display similar Rb-O distances within the first sphere for both the ion-exchanged soda-lime and the disilicate glasses ($r_{\text{Rb-O}} \approx 2.80$ Å). This value is in agreement with bond lengths determined for both rubidium silicate glasses and crystals [7,8]. The EXAFS data indicate a decreased coordination number at the glass samples. Furthermore, the second coordination shell does not correspond to that of usually melted glasses. Structural rearrangements could be observed only in the second sphere at higher temperatures (600°C) indicating a tendency towards the disilicate structure. These results make clear the difference in comparison with the behaviour of silver ions which generate their own environment immediately during the ion exchange at lower temperatures.

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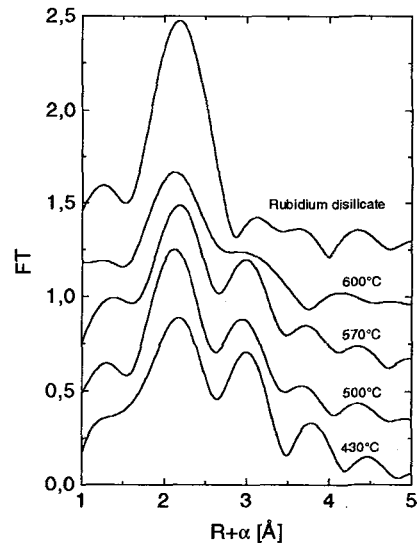


Figure 3: Fourier transforms of Rb K-edge spectra of ion-exchanged glasses compared with disilicate glass

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