Structure of oxide glasses by X-ray diffraction: Li$_2$O-V$_2$O$_5$-B$_2$O$_3$ and Nb$_2$O$_5$-NaBO$_2$-NaPO$_3$ glasses

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Two series of multi-component oxide glasses were studied by total X-ray diffraction experiments (XRD). The photon energy chosen for the experiments on BW5 in May 2011 was 120.0 keV. The range of scattering vector $Q$ with $0.5 \leq Q \leq 340$ nm$^{-1}$ is covered with comparably small scattering angles which allow simple absorption corrections. Various additional absorbers and variable slit widths of the detector help to avoid strong dead-time effects and maximize the available scattering intensity because the count rates decrease for several orders of magnitude with increasing scattering angles. Additionally, the incoherent scattering (Compton effects) limits the statistical accuracy of the data at large $Q$. The energy window of the Ge-detector removes possible fluorescence from Nb. The beam size used is 1 x 4 mm$^2$. The filling rate of the capillaries of diameters 3 mm with the powders prepared from the flakes of the Li$_2$O-V$_2$O$_5$-B$_2$O$_3$ glasses is considerably less than that of a dense packing. Accordingly, small intensities limit the useful maximum $Q$ to 250 nm$^{-1}$ (cf. Fig. 1a). Differently, the capillaries (2 mm) filled with the coarse-grained powders of the Na$_2$O-Nb$_2$O$_5$-P$_2$O$_5$-B$_2$O$_3$ glasses show excellent scattering with useful data up to $Q_{\text{max}}$ of 340 nm$^{-1}$ (cf. Fig. 2a).

The series of Li$_2$O-V$_2$O$_5$-B$_2$O$_3$ glasses starts with the binary V$_2$O$_5$-B$_2$O$_3$ ($R = 0.0$) sample that is unfortunately partially crystallized and not suitable for further quantitative analysis. The first peak in the correlation function, $T(r)$, belongs to the B-O bonds and does not change with the Li$_2$O content. The second peak belongs to the V-O distances. Its first component at 0.165 nm increases with increasing Li$_2$O content at the expense of distances at 0.180 nm whereby the total V-O coordination number determined does not change. The Li-O peak at ~0.20 nm is very small and cannot be analysed. The visible ripple in this range results from the Fourier transform. The number of oxygen neighbours of Li used when fitting the peaks is four. The subsequent peak at 0.24 nm is attributable to the O-O edges of the BO$_3$ triangles. The V-O distances of Li$_2$O-V$_2$O$_5$-B$_2$O$_3$ glasses cannot be obtained by neutron diffraction due to very small coherent scattering of vanadium. For X-rays, vanadium is the strongest scatterer of the samples studied. Detailed results are extracted.

![Figure 1](image-url)
The second series of multi-component glasses are additions to a recent work where the Nb-O distances of NbO$_6$ octahedra are analysed in dependence on compositions of the Nb$_2$O$_5$-NaPO$_3$ glasses [1-3]. One corner of the NbO$_6$ is formed of a doubly-bonded oxygen. This effect is interpreted as a specialty of the presence of PO$_4$ tetrahedra with overbonded P-O and underbonded Nb-O in P-O-Nb bridges. The Nb=O bonds change for greater Nb$_2$O$_5$ content because Nb-O-Nb bridges with single Nb-O bonds reduce the excess of valence on the octahedral Nb sites.

Here, two Nb$_2$O$_5$-NaPO$_3$ compositions with Nb$_2$O$_5$ contents of 0.1 (1) and 0.3 (4) are chosen as the starting glasses where the second sample is expected to have considerable numbers of Nb-O-Nb bridges. The substitution of B for P should reduce the tendency to form Nb=O bonds. Therefore, excellent scattering data are needed which allow resolving the different Nb-O bonds. The maximum quality of scattering data that is achieved at BW5 is obtained with a $Q$-range of $0.5 \leq Q \leq 340$ nm$^{-1}$ (cf. Fig. 2a). In prior XRD, we used $Q_{\text{max}} = 310$ nm$^{-1}$ for obtaining excellent data of vitreous P$_2$O$_5$ [4]. The Fourier transforms shown in Fig. 2b are obtained from the $S(Q)$ in the full $Q$-range and without damping. Some ripples of the $T(r)$ are due to termination effects and noisy data at large $Q$. The visible changes at ~0.180 nm between the P-O and Nb-O peaks are of most interest. The analysis needs taking into account the termination ripples as it was used for modelling the B-O and V-O peaks shown in Fig. 1b.

The lower $S(Q)$ of sample (7) shown in Fig. 2 belongs to a singular sample. Glass forming of the binary system is restricted to this compositional point. The structure of this glass seems comparably simple with only NbO$_6$ and PO$_4$ units. The groups are linked with each other via corners whereby Nb-O-Nb and Nb-O-P bridges occur. Possibly, some three-coordinated oxygens exist. The analysis of the glasses will become more reliable by including neutron diffraction. Such experiments are planned in the near future.

Figure 2: Nb$_2$O$_5$-NaPO$_3$ glasses with increasing NaBO$_2$ fractions (downwards). (a) Structure factors – the upper curves belong to small series of four-component glasses – the lower curve belongs to a binary glass. (b) Correlation functions in the range of the first-neighbour distances. The B-O distances are small contributions on the left flank of the P-O peak. The Na-O distances are larger than Nb-O bond lengths. They form a broad distribution and interfere with O-O peaks. Spurious ripples are due to noise and termination at $Q_{\text{max}}$.

References