Structure of Na$_2$O-GeO$_2$-P$_2$O$_5$ glasses by X-ray and neutron diffraction

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The Ge-O coordination number ($N_{\text{GeO}}$) is 4 in vitreous GeO$_2$. The mixed network former GeO$_2$-P$_2$O$_5$ glasses show an increase of the Ge-O coordination number ($N_{\text{GeO}}$) with increasing P$_2$O$_5$ content due to the asymmetric distribution of bond valencies in the favored P-O-Ge bridges [1]. Large $N_{\text{GeO}}$'s with ~5 were obtained in K$_2$O-GeO$_2$-P$_2$O$_5$ glasses [2]. The origin of this $N_{\text{GeO}}$ increase differs from that of the germanate anomaly where the absence of non-bridging oxygen is related to the increase of $N_{\text{GeO}}$.

The Na$_2$O-GeO$_2$-P$_2$O$_5$ glasses here investigated possess larger P$_2$O$_5$ contents than the samples used before [2]. The structural features of the samples are determined by X-ray and neutron diffraction experiments of excellent resolving power. The strong X-ray scattering of Ge and sufficiently different lengths of the P-O and Ge-O bonds allow to resolve the Ge-O peak and to extract $N_{\text{GeO}}$. The resulting values vary in a range 4.5 $\leq N_{\text{GeO}}$ $\leq$ ~6. $N_{\text{GeO}}$ depends on the P$_2$O$_5$ content. Its maximum value is obtained for the sample of only 20 mol% GeO$_2$.

The pre-peaks in the structure factors $S(Q)$ at position $Q_1 = \sim 8$ nm$^{-1}$ that were reported earlier [2] appear also in all the $S(Q)$ of the present glasses. This pre-peak is related to a length of medium-range order of ~1.0 nm. The distance is explained with the mutual order of micro-domains of alkali-phosphate and Ge-phosphate regions [2]. The shape of the pre-peak and its position at $Q_1$ are widely independent of the GeO$_2$ content. This model gets support from other authors who reported a combined NMR and X-ray photoelectron spectroscopy study of GeO$_2$-NaPO$_3$ glasses [3] The preferred attraction of Na$^+$ ions by the phosphorus component and the favored P-O-Ge linkages agree with our model assumptions.