Structure of Na_2O-GeO_2-P_2O_5 glasses by X-ray and neutron diffraction

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The Ge-O coordination number (N_{GeO}) is 4 in vitreous GeO_2. The mixed network former GeO_2-P_2O_5 glasses show an increase of the Ge-O coordination number (N_{GeO}) with increasing P_2O_5 content due to the asymmetric distribution of bond valencies in the favored P-O-Ge bridges [1]. Large N_{GeO}'s with ~5 were obtained in K_2O-GeO_2-P_2O_5 glasses [2]. The origin of this N_{GeO} increase differs from that of the germanate anomaly where the absence of non-bridging oxygen is related to the increase of N_{GeO}.

The Na_2O-GeO_2-P_2O_5 glasses here investigated possess larger P_2O_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_{GeO}. The resulting values vary in a range $4.5 \leq N_{GeO} \leq \sim 6$. N_{GeO} depends on the P_2O_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 = ~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.

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