ΔΙΑΛΕΞΗ

“Preferential bonding, clustering, and phase-separation in borosilicate and Mn-borate glasses – a multi spectroscopic approach”

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Preferential bonding, clustering, and phase-separation in borosilicate and Mn-borate glasses – a multi spectroscopic approach

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In low alkali borosilicate glasses, preferential bonding but also visible phase separation with physical interfaces are known to occur. Therefore, not only the question of the fraction of four- and three-fold coordinated boron deserves special consideration, but also the connectivity of the tetrahedral and trigonal borate groups with each other and with the silicate network. Older structural studies and models of borate and borosilicate glasses often invoke rules, which will be critically reconsidered.

While the addition of small amounts (~1mol%) of Al$_2$O$_3$ can prevent phase separation in low alkaline borosilicate glasses, vibrational and 2D NMR spectroscopy show a preference for B-O-B and Si-O-Si bonds over mixed B-O-Si bonds when the samples are properly annealed. More interestingly, while rapidly quenched samples show both B$_4$-O-Si and B$_3$-O-Si bonds (with B$_2$ and B$_3$ denoting four- and three-fold coordinated boron, respectively), the number of mixed bonds decreases significantly in annealed samples and, of the remaining mixed bonds, B$_3$-O-Si links are strongly favoured over B$_4$-O-Si bonds.

Addition of small amount of MnO to a duran glass, converts neutral BØ into charged metaborate [BØ]$^4_-$ tetrahedra that bond preferentially to borate rather than to silicate entities. Clustering of Mn$^{2+}$ ions near [BØ]$^4_-$ tetrahedra induce a transition from preferential bonding to finally visible phase separation. The increased clustering of Mn$^{2+}$ ions can be followed by electron spin resonance and photo-luminescence spectroscopy. In order to follow MnOn-clustering at higher concentrations the (1−2x)MnO−x(SrO–B$_2$O$_3$) system was studied. Here, borate rings consisting of three tetrahedral orthoborate units, [BØ$_2$O$_3$]$^3_-$, were identified by vibrational spectroscopy. These rings strengthen the glass network and a second boron oxide anomaly is observed by an increase in the glass transition temperature at very high metal oxide contents.