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## Structural aspects of the mixed-ion effect in phosphate glasses

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SP; (2) Institut für Physikalische Chemie, Westfälische Wilhelms-Universi The mixed-ion effect (or mixed-alkali effect) is the dramatic non-linear reduction in the values of transport properties in glasses due to restriction in ionic mobility upon mixing. A satisfactory explanation of this phenomenon has been elusive during five decades. Metaphosphate glasses AxB1-xPO3 with two mobile monovalent cations A+ and B+ are archetypical systems for analysis of the mixed-ion effect in d.c. conductivity, which is strongly dependent on the nature of the mixed chemical species. The deepest known reduction in conductivity is observed in Rb-Li metaphosphates, attaining 8 orders of magnitude. In contrast, reductions of only 1 order of magnitude are observed in Ag-Na metaphosphates. In the first part of this lecture, recent significant experimental and theoretical developments in the understanding of the mixed-ion effect will be reviewed. In particular, the relevance of the structural properties of the glass on the manifestation of the effect will be discussed. On the second part of the lecture, a recent systematic analysis of local order and the alkali distribution in mixed metaphosphates will be presented, covering glasses with A-B pairs as Na-Li, Na-Ag, Na-K, Na-Rb, Na-Cs, and Li-Rb, Li-Cs, Ag-Cs. The aim to of this study is the identification of segregation or random mixture of cation species and their possible dependence with the cation size mismatch or differences in ionic potential. A broad set of Nuclear Magnetic Resonance (NMR) techniques were applied: 31P, 23Na, 7Li and 133Cs high-resolution NMR, 109Ag-NMR, 23Na Triple-Quantum-MAS NMR, REDOR between 31P, 23Na, 7Li and 133Cs, 87Rb quadrupole Carr-Purcel-Meiboom-Gill, and 23Na-NMR spin-echo decay. The structural picture emerging from these results reveals the similarity in local environments around each kind of alkali, irrespective of the substitution ratio. A common structural adjustment on the cation environment was discovered, consisting in the compression of the oxygen environment around the smaller cation of the pair as their concentration is reduced. The compression causes an increase in the local symmetry of the coordination polyhedra. The set of results show also a mixture of cations species at atomic scale. However, the 23Na-23Na magnetic coupling reveals that this mixing is not statistical, existing a detectable like-cation preference at short range for some systems (Na-K, Na-Cs). These findings support recent structural approaches used to calculate the diffusion pathways for the mobile cations, indicating the possible generalization of these models of the mixed-ion effect to many other glass systems.