Ca and Sr Bonding in Mixed Phosphate Glasses

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Abstract

Incorporation of Sr to Ca-phosphate bioglasses opened many possibilities for clinical applications. The cation release in physiological conditions is influenced at atomic scale by the interactions with the glass forming groups. To analyze the cation structural preferences in the glass network, two series of mixed polyphosphates glasses were studied: (I) Na-Ca-Sr w Na2O (0.57-w-x) SrO x CaO 0.43 P2O5 ($0 \leq w \leq 0.40$, $0 \leq x \leq 0.40$), and (II) (0.50-x-y) Li2O y Cs2O x SrO 0.50 P2O5 ($0 \leq x \leq 0.40$, $0 \leq y \leq 0.50-x$). 31P, 23Na, 7Li and 133Cs nuclear magnetic resonance techniques were applied to analyze local structure around phosphate groups and cation sites. For polyphosphates with one alkaline earth, transitions in the evolution of properties (molar volume, glass transition temperature, 31P resonance of chain-end tetrahedra) were detected as a function of the alkaline earth content, which can be interpreted in terms of preferential bonding of the divalent cation to the O in (PO3.5)2- anions (Q1), instead of (PO3)- (Q2). This non-statistical bonding to the available O is only possible up to a maximum concentration of the alkaline earth oxide, calculated as $x = 0.28$, in good agreement with the observed break in properties in Na-Sr polyphosphate ($x = 0.30$). A similar behavior seems plausible for Ca2+ in Na-Ca polyphosphate, but changes in the medium range order and progressive structural distortions induced by the stronger ion cause smooth variations of the molar volume. The systematic variation of the Sr/(Sr+Ca) allowed to observe the transition between these two structural regimes. In series (II), Sr was introduced to perturb the Li-Cs mixed alkali effect. The analysis of the nuclear dipolar couplings shows that both alkalis are randomly dispersed, irrespective of the concentration of Sr. All NMR parameters are scaled by the alkali atom concentration, irrespective of the element (Sr, Li, Cs) used to dilute the alkali, revealing the random mixture of these three species in the metaphosphate matrix.

Keywords: phosphate glasses, mixed alkali effect, glass structure, nuclear magnetic resonance

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