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Alkali cation effect in molybdenum phosphate glass: Structure and crystallization study by solid state NMR and Raman scattering

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Vitreous and ceramic samples in the system $(1-x)$ $\text{MPO}_3 - x\text{MoO}_3$ with $(\text{M}=\text{Na}, \text{K} \text{ and } \text{Rb})$ were prepared and investigated in the concentration range $(0 \leq x \leq 0.7)$. The structural study of these glasses and ceramic network was monitored as a function of the MoO_3 concentration by Raman scattering and ^{31}P solid state nuclear magnetic resonance. The ^{31}P MAS-NMR data differentiate between species having two, one, and zero P-O-P linkages ($\text{Q}(2)$, $\text{Q}(1)$, and $\text{Q}(0)$ species), respectively. Interatomic connectivities involving these units are revealed by two-dimensional INADEQUATE data, through the formation of double quantum coherences mediated by indirect ^{31}P - ^{31}P spin spin interactions via P-O-P linkages. As this method discriminates against isolated P atoms, it also serves as an important spectral editing tool for constraining lineshape fits. Incorporation of MoO_3 into alkali metaphosphate glasses results in dramatically increased glass transition temperatures, suggesting that the glass structure is affected by strong mixed-network former effects. ^{95}Mo and ^{31}P NMR data and Raman spectra suggest that the Mo species are most likely six-coordinate. A substantial new insight into the structure of alkali metaphosphate glasses modified by molybdenum oxide based on the comparison of the glass and ceramic spectra with those on the model compounds ($\text{MMoO}_2\text{P}_2\text{O}_7$ and MMoO_2PO_4), the intermediate steps as the $\text{MoO}_3/\text{MPO}_3$ ratio is increased. Based on this working assumption, the ^{31}P MAS NMR spectra have been interpreted in terms of the various types of phosphate species with different P-O-P and P-O-Mo connectivities are invariant with alkali cation.