08-064

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

S. H. Santagneli(1), Jinjun Ren(2), Matthias T. Rink(2), Sidney J.L. Ribeiro(1), Younes Messaddeq(1) , Hellmut Eckert (2)

1 Laboratory of Photonic Materials, Institute of Chemistry – UNESP, Brazil ; 2 Institut für Physikalische Chemie, Westfälische Wilhelms-Universität Münster

Vitreous and ceramic samples in the system (1-x) MPO3 – xMoO3 with (M=Na, K and Rb) were prepared and investigate in the concentration range (0 ? x ? 0.7). The structural study of these glasses and ceramic network was monitored as a function of the MoO3 concentration by Raman scattering and 31P solid state nuclear magnetic resonance. The 31P MAS-NMR data differentiate between species having two, one, and zero P-O-P linkages (Q(2) Q(1), and 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 31P-31P 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 MoO3 into alkali metaphosphate glasses results in dramatically increased glass transition temperatures, suggesting that the glass structure is affected by strong mixed-network former effects. 95Mo and 31P 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 (MMoO2P2O7 and MMoO2PO4), the intermediate steps as the MoO3/MPO3 ratio is increased. Based on this working assumption, the 31P 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.