Silver borophosphate glasses modified with tungsten and molybdenum oxide

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This contribution deals with study of mixed glass former effect (MGFE) and its effects in two series of borophosphate glasses of $40Ag_2O$-$20MO_3$-$(40\text{-}x)P_2O_5$-xB_2O_3 (where M = W, Mo) in a composition range of x = 0-30 mol% B_2O_3. Basic physico-chemical properties were determined, and thermal properties studied by differential thermal analysis and thermomechanical analysis. The glass structure was investigated using Raman spectroscopy and both 1D and 2D ^{11}B and ^{31}P MAS NMR spectroscopy. Behavior and oxidation states of tungsten and molybdenum throughout the series was investigated using EPR spectroscopy. The electrical properties of the glasses were obtained by using impedance spectroscopy.

In both series, glass transition temperature, T_g, increases in range of 0-10 mol% B_2O_3, further additions results in slight decline of T_g values. Results from impedance spectroscopy reveal non-linear increase in DC conductivity which can be attributed to MGFE and therefore changes in the structure of the glass network. The second possible explanation of the development in DC conductivity can be attributed to the presence of reduced forms of W and Mo which can affect the resulting conductivity by the polaron hopping phenomenon. This phenomenon has already been studied and confirmed on glasses of similar systems [1].

Structure of the glasses was probed with multiple MAS NMR experiments. To get first information about the glass network, standard 1D experiments of ^{11}B and ^{31}P nuclei were performed. From obtained ^{31}P MAS NMR spectra is visible the transformation of the dominant phosphate structural units in the direction of Q^2->Q^0 with B_2O_3 additions, and thus the shortening of the phosphate chains. Development in ^{11}B MAS NMR spectra reveals presence of both BO_4 and BO_3 structural units through the series. Interconnections between phosphate and borate species was further studied by multiple 2D correlation techniques. Namely 2D ^{31}P INADEQUATE sequence was used to probe direct trough bond connections between phosphate structure units, which confirmed shortening of phosphate chains. As next was done investigation of the P-O-B linkages using the ^{11}B(^{31}P) D-HMQC sequence. This experiment confirmed presence of both P-O-B$^{[4]}$ and P-O-B$^{[3]}$ structure units connection inside the glass network. And lastly 2D ^{11}B DQ-SQ sequence was used to investigation of presence and nature of B-O-B bonds. This experiment reveals presence and evolution of all three BO_3-BO_3, BO_3-BO_4 and BO_4-BO_4 pairs inside the glass network. By combining all these methods, we were able to prepare an approximate structural model of these glasses, which could be used to explain the macroscopic properties of the studied glasses.

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[1] A. Šantić, J. Nikolić, S. Renka, et al., Solid State Ionics, 2022, 375, 115849.