

Silver phosphate glasses modified by transition metal oxides

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Phosphate glasses of the systems $\text{Ag}_2\text{O-V}_2\text{O}_5\text{-WO}_3\text{-P}_2\text{O}_5$ and $\text{Ag}_2\text{O-V}_2\text{O}_5\text{-Nb}_2\text{O}_5\text{-P}_2\text{O}_5$ were studied. In two compositional series of $40\text{Ag}_2\text{O-xV}_2\text{O}_5\text{-(1-x)WO}_3\text{-30P}_2\text{O}_5$ and $40\text{Ag}_2\text{O-yV}_2\text{O}_5\text{-(1-y)Nb}_2\text{O}_5\text{-30P}_2\text{O}_5$ 13 glasses were prepared and studied. Starting glasses without V_2O_5 are slightly yellowish. Glasses with vanadium oxide V_2O_5 are black due to the presence of vanadium in the form of V^{4+} . Thermal analysis showed on decreasing glass transition temperature with an increasing V_2O_5 content in both studied series. For the glass series with WO_3 glass transition temperature varies within the values $392\text{-}279^\circ\text{C}$, for Nb_2O_5 containing glasses within the values of $572\text{-}279^\circ\text{C}$. Glass structure was studied by Raman spectroscopy and by ^{31}P MAS NMR. The NMR spectra of $40\text{Ag}_2\text{O-xV}_2\text{O}_5\text{-(1-x)WO}_3\text{-30P}_2\text{O}_5$ glass series contain one broad resonance peaking at $-4.2 - +3.1$ ppm. Such position of the resonance signal corresponds to the presence of Q^1 diphosphate structural units. For the $40\text{Ag}_2\text{O-yV}_2\text{O}_5\text{-(1-y)Nb}_2\text{O}_5\text{-30P}_2\text{O}_5$ glass series ^{31}P NMR spectrum of the glass with $y = 0$ evidently consists of two resonances, which indicates the presence of two types of phosphate units of Q^1 and Q^0 . Such shape of the NMR spectrum is ascribed to the formation of Nb-O-Nb-O-Nb chains from niobate octahedra in the starting glass. These chains disappear with a decrease in the Nb_2O_5 content in the glasses. Raman spectrum of the starting tungstate-phosphate glass series $40\text{Ag}_2\text{O-xV}_2\text{O}_5\text{-(1-x)WO}_3\text{-30P}_2\text{O}_5$ with $x = 0$ reveals the dominant band of 918 cm^{-1} , the position of which shifts slightly to lower wavenumbers with decreasing WO_3 content. This band was ascribed to the vibrations of the W-O bonds in WO_6 octahedra. Raman spectrum of the $40\text{Ag}_2\text{O-yV}_2\text{O}_5\text{-(1-y)Nb}_2\text{O}_5\text{-30P}_2\text{O}_5$ glass without V_2O_5 is composed of two bands. The first band at 805 cm^{-1} was ascribed to the presence of Nb-O-Nb-O-Nb chains and the second band at 896 cm^{-1} to the vibrations of Nb-O bonds in NbO_6 octahedra. Final glass with V_2O_5 only reveals in the Raman spectrum dominant band at 912 cm^{-1} , assigned to the vibrations of O-V-O bonds in vanadate structural units.