Phosphate glasses modified with transition metals

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Phosphate glasses present an important group of glass materials having several commercial applications. The most important applications of these glasses are laser glasses, glasses for the deposition of radioactive wastes, and glass solders. Nd-doped laser glasses are produced and tested for the application in fusion reactors. For the storage of radioactive wastes, Fe_2O_3-P_2O_5 glasses were proposed due to their high chemical durability and the ability to include a high content of radioactive oxides. Glasses of the ternary system SnO-ZnO-P_2O_5 were investigated for the application in solders replacing lead-based glasses. These glasses reveal a sufficient chemical durability, low values of the glass transition temperature and a low coefficient of thermal expansion.

Our studies of ternary phosphate glasses were devoted mainly to three transition metal oxides MoO_3, WO_3 and Nb_2O_5, which are able to form large glass forming regions in various ternary systems. These studies will be demonstrated on two ternary systems BaO-MoO_3-$P_2O_5$and BaO-Nb_2O_5-P_2O_5.

Structure of glasses in the BaO-MoO_3-P_2O_5 ternary system was studied by Raman and ^{31}P NMR spectroscopies. The glass-forming region in the ternary system was determined, and stable glasses with 0-70 mol% MoO_3were obtained. From the NMR and Raman spectra of glasses, a structural model was proposed. Structural network contains mostly MoO_6 octahedra and PO_4 tetrahedra. In glasses with a high MoO_3 content, the presence of a broad Raman band 854 cm^{-1}, ascribed to Mo-O-Mo bonds, showed on the formation of clusters composed of MoO_6 units. MoO_6octahedra prevailed in the glass structure, similarly to crystalline MoO_3 and to the compound $Ba(MoO_2)_2(PO_4)_2$. Formation of MoO_4 tetrahedra was proposed in the glasses with a low P_2O_5 content.

Phosphate glasses of the ternary system BaO-Nb_2O_5-P_2O_5 were studied in two compositional series with a constant BaO or Nb_2O_5 content. Chemical durability of the Nb_2O_5-containing glasses is high and the glass transition temperature increases significantly with increasing Nb_2O_5 content as well as the index of refraction. According to the Raman spectra at low Nb_2O_5 content niobium forms isolated octahedra NbO_6 incorporated in the glass network, but when Nb_2O_5 content increases, these octahedra are linked into chains and further into three-dimensional clusters. NbO_6 octahedra clustering is reflected also in the ^{31}P MAS NMR spectra.

Study of the glass to crystal transformation was realized for two ternary compounds in the glass-forming region of the BaO-Nb_2O_5-P_2O_5 system: $Ba_3Nb_2(PO_4)_4O_2$ with 16.66 mol% Nb_2O_5 (glass composition $3BaO.1Nb_2O_5.2P_2O_5$) and $BaNb_2P_2O_{11}$ with 33.33 mol% Nb_2O_5 (glass composition $1BaO.1Nb_2O_5.1P_2O_5$).

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