Effect of titanium dioxide on thermal behavior and properties of niobate-phosphate glasses

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Niobium is one of the elements used to modify the structure and properties of phosphate glasses. It was found that niobium containing phosphate glasses show good chemical durability, good VIS to near IR transparency, high transition temperature and high refractive index. These properties contribute to their prospective applicability for various optical devices or as potential candidates for the nuclear waste immobilization. Moreover, niobate-phosphate glasses show also promising biological response with stimulation of alkaline phosphatase activity of osteoblast-like cells. The previous results indicated that the incorporation of larger amounts of Nb_2O_5 into phosphate glasses requires the addition of stronger bases like alkali or alkaline earth oxides. TiO_2 is used as a nucleating agent in silicate glasses, nevertheless recent studies indicate that the TiO_2 addition can markedly improve properties of the phosphate glasses and glass-ceramics, e.g. chemical durability, thermal, mechanical and optical properties.
TiO_2 containing phosphate-niobate glasses were prepared in the compositional series $40Na_2O$-$40P_2O_5$-$20Nb_2O_5$+xTiO_2 within the range of x=0-36, using conventional melt quenching technique, when the melt (1200-1400 ^oC) was poured into a tempered graphite mould. Glasses were characterized by the measurements of density, molar volume and chemical durability. The structure of glasses was investigated by Raman spectroscopy, their thermal properties were studied by DSC, thermodilatometry and hot stage microscopy. Crystalline phases were identified by X-ray powder diffraction analysis.
Raman spectra showed that the structure of starting $40Na_2O$-$40P_2O_5$-$20Nb_2O_5$ glass is formed mainly by metaphosphate (Q^2) and diphosphate (Q^1) structural units interconnected by $P-O-P$ bonds. Nb_2O_5 is incorporated in the structural network in the form of NbO_6 octahedral units. Introducing and gradually increasing of TiO_2content causes a slow depolymerization of the phosphate structural network and the development of probably TiO_6 octahedral units in the local structure of the glass matrix. Glasses show the almost linear increase in the density, whereas molar volume steeply decreases with increasing TiO_2 content. The highest values of glass transition temperature, dilatometric softening temperature, crystallization temperature and flow temperature were obtained for the glass containing 28 mol% TiO_2. This glass revealed also the highest chemical durability against water attract and on the contrary the lowest thermal expansion. The DSC curves indicated that all glasses crystallize on heating.

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