THE ROLE OF FLUORINE IONS IN THE FORMATION SILICA GEL AND GLASS STRUCTURE

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Fluorine-containing silica gels can be used as precursors of unhydrous glasses for radiation hard fiber optics. The silica gels were prepared by the sol-gel process including following stages: hydrolysis of tetraethylorthosilicate (TEOS) in a four-component system $Si(OC_2H_5)_4$ – C_2H_5OH – H_2O – HCl, adding the fumed silica (aerosil) into the sol, sonoactivation, centrifugal separation, neutralization by the ammonia solution, gelation, washing the gels in distilled water, drying and fluorination the xerogels by the procedure of heating in the freon/oxygen atmosphere. Fluorinated gels were consolidated into transparent silica glass in the atmosphere of helium gas at the temperature 1200-1300^{0}C. SEM and AFM analysis BET surface area investigations were used for characterization of the xerogels and glasses morphology.

The pore volume increases until heating up to 800 ^{0}C and when the temperature rises up to 1100 ^{0}C the process of pore collapse is began, resulting in 1.6% porosity. At the temperature 1200 ^{0}C the pores are eliminated and the density becomes equivalent to fused silica.

There is a little change in the pore distribution of the hybrid silica gels until heating to the interval 800–1100 ^{0}C. Densification primarily is due to only the number of pore decreasing.

The pore-size distribution of fluorinated gels has a trimodal character: the network contains micropores (3.0 nm), mezo – and macropores (5.0–25.0 nm). The pore size can been larged by chemical attack of silica network with fluorine ions in vapor phase until heating and dissociation of ammonium fluoride.

Some fluorine-containing compounds (HF, NH_4F, NH_4HF_2, CF_2Cl_2, $C_2F_3Cl_3$ etc.) can to react with surface hydroxyl groups and gel silica network at elevated temperature, replacing OH-ions and forming the fluorine-containing volatile substances (SiF_4, SiF_3).

The process of gas-phase fluorine doping reduces hydroxyl level in the dense silica glass to below 3–5 ppm. The contents of fluorine determined by the MXRSA is 0.4–0.45% by weight. Such glasses have about 90% transmission at 3671 cm^{-1} (hydroxyl group absorption) region. The gas-phase doped sample containes also the chlorine contamination in the level of 0.17% by weight.