

RAMAN AND EDX STUDIES OF FLUORINE-DOPED SILICA GLASS

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Fluorine doping of silica (SiO₂) glass is widely used in optical fiber industry to depress the refractive index in fiber cladding layers. Additionally, fluorine doping increases the deep-UV (<190 nm) transparency and the resistance to ultraviolet solarization or to ionizing irradiation. This effect is attributed to removing the glassy disorder-induced point defects by F-doping. Fluorine enters silica mainly as Si-F groups bounded to tetrahedrally coordinated Si atoms in glass network. They do not create states in the gap and their concentration can be assessed by the intensity of their Raman band at ~930 cm⁻¹. However, the published F-concentration / Raman intensity data are not mutually consistent. This study reports parallel Raman and energy dispersive X-ray microanalysis (EDX) studies of F-doped (0 to ~ 7 wt%) silica glasses produced by industrial plasma-deposition or by sol-gel methods. For reliability of quantitative EDX analysis data, standard reference samples consisting of pressed SiO₂ and LiF nanoparticles were used as a reference.

Recently a new radiation-induced point defect in heavily F-doped silica was reported: a dangling paramagnetic silicon bond on silicon, coordinated by 2 oxygens and a fluorine atom [1]. This finding may hint to the presence of a SiF₂ group – Si coordinated by 2 oxygens and 2 F atoms - as the most probable precursor of this defect. The Raman spectrum of SiF₂ groups in silica has not been reported. DFT calculations (ORCA package) indicate that the expected splitting between symmetric and antisymmetric SiF₂ vibration mode frequencies is of order 70 cm⁻¹. Our Raman measurements of strongly F-doped silica show a significant broadening (increase of fwhm halfwidth from 28 cm⁻¹ to 45 cm⁻¹) and change of shape of fluorine-related band. Apart from the possible relation to SiF₂ groups this indicates that the concentration-related change of the shape of Si-F Raman band must be accounted for when employing this band for fluorine concentration monitoring.

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References

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