Scattering and structural relaxation in silica glass and optical fibers preforms

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These last years have seen great improvement in optical fibers transmission, partly due to very low impurities (OH) concentrations achieved. Indeed, losses in fibers originate from infra-red absorption but also from light scattering strongly dominated by Rayleigh scattering.

Glass can be considerated as a frozen liquid, and contains density and concentration fluctuations which have been frozen-in during the liquid fast cooling. Those fluctuations give rise to elastic light scattering depending on of structural freezing temperature, this parameter is called fictive temperature and charaterize the glass.

In a first part of this study, we have focused on density fluctuations evolution versus fictive temperature in silica glass. Short and medium range structure versus fictive temperature has been the topic of several studies, [1, 2, 3] in glasses having different compositions. In order to understand the effect this parameter on silica glass structure, we have made several Raman and Infra-Red spectroscopic measurements on the same silica glass (all the sample having different fictive temperatures come from the same original sample) to obtain some equation governing the evolution of different spectroscopic signatures [4, 5] :

- 440cm^{-1} Raman band shifts toward high frequencies : Si-O-Si mean angle reduction in 5-6-7 membered rings
- D_1 et D_2 sharp peaks intensity increase : inceasing number of 3 and 4 membered rings with increasing fictive temperature
- 1120 cm^{-1} and 2260cm^{-1} infra-red absorption bands shift toward low frequencies : Si-O-Si mean angle reduction

These laws alow us to estimate the fictive temperature of our initial sample and of samples annealed at low temperatures. We also compared each signature (and the associated structural element) relaxation time for samples annealed at the same temperature but during different times.

Rayleigh scattering measurements [4, 5, 6] can be compared with small angle X ray scattering (SAXS), zero angle X-ray intensity depending on static and dynamic density fluctuations. Moreover, it is possible to measure *in-situ* density fluctuations while increasing

temperature in SAXS, and to focus on thermal history consequences on structural relaxation in the glass transition region. [7, 8].
Silica glass is densified under fictive temperature increase, Si-O-Si angles decrease in 5-6-7 tetrahedra rings, some of them are broken to create new small 3 and 4 membered rings. Such structural modifications are bound to medium range structure : on one part, inhomogeneities such as "density fluctuations " increase with increasing fictive temperature. On the other part, nanostructures responsible for the Boson Peak are modified in such a way that the peak shifts toward higher frequencies. Finally, in this silica glass, it appears possible to decrease 15% of Rayleigh scattering losses while decreasing fictive temperature.

The second step of optical preforms studies consists in studing core composition glass : germanium doped silica (germanium increase refraction index of silica glass). Doping glass has two effects : the glass transition temperature is decreased, which should decrease density fluctuations but dopants give rise to concentration fluctuations and a strong contribution to Rayleigh scattering losses. Density and concentration fluctuations have been measured in this glass using small angle X-ray scattering.

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