ESRF	**Experiment title:** Rare-earth distribution and local structure in rare-earth silicate fibre preforms	**Experiment number**: CH-640
Beamline: ID26	**Date of experiment**: from: 12/4/99 to: 19/4/99	**Date of report**: 21/7/99
Shifts: 21	**Local contact(s)**: Riccardo Signorato, Christophe Gauthier	*Received at ESRF:*

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Report: Rare-earth doped silicate fibres are important in the telecommunications, sensor and opto-electronics industries on account of their use in fibre amplifiers and lasers. The physical and optical properties arise from the rare-earth components in these materials since their complex electronic structure allows a wide range of available energy states to be exploited. In order to understand further these properties, the rare-earth structural environment was probed using EXAFS, ID26 being crucial for the experiment since (i) the rare-earth ions exist in such low concentrations (0.2-4 wgt% R_2O_3); (ii) the structure was probed as a function of radial distance (in 100 μm steps) from the preform core.

Rare-earth L_{III}-edge EXAFS data for two neodymium and three erbium containing fibres were obtained and the germanium K-edge was probed (germanium being a 15-18wgt% co-dopant) for one sample in order to obtain EXAFS data consistent with previous work [1]. One of the erbium samples was chosen to investigate the structure as a function of radial distance from the preform core and here six EXAFS spectra were obtained at 100 μm intervals from the core centre.

The Ge EXAFS results confirmed the expected immediate four-fold oxygen coordination and second neighbour tetrahedral silicon at respective distances of 1.69Å and 2.61Å.

The L_{III}-edge EXAFS results revealed a split nearest-neighbour oxygen shell at distances of ~2.05/2.40Å and ~2.10/2.25Å from the Nd^{3+} and Er^{3+} ions respectively with corresponding coordination numbers of approximately 1 and 5, i.e. overall resembling an octahedral rare-earth environment. A similarly split second neighbour silicon shell at distances of ~2.8/3.8Å was observed for the neodymium samples. Such distances suggest that five of the six oxygens are branching (average Nd-O-Si angle = 145°) whilst the other one subtends a Nd-O-Si angle of approximately 100°. Such an angle is indicative of a covalently bonded oxygen atom, its two lone pairs reducing the otherwise tetrahedral (109.5°) angle to the observed value. This level of covalency would explain the markedly short Nd-O distance. Moreover, the tendency for covalency of one of the rare-earths ligands can be rationalized by the fact that the Nd^{3+} ion comprises an odd number of electrons in the 4f-shell, which the more usual coordination of oxygen atoms to a metal centre, involving a dative contribution of an oxygen lone pair, would not be able to make even.

The second neighbour shell of one of the erbium samples (1wgt% Er_2O_3, 15wgt% GeO_2) was modelled in a similar fashion. However, it was not possible to model the erbium sample with lower rare-earth content (0.3wgt% Er_2O_3, 18wgt% GeO_2, 1wgt% Al_2O_3) in the same manner. Instead, the data fitted well with germanium in the second neighbour shell at a distance of ~3.3Å from erbium. The closest distance from erbium at which silicon could be modelled is 3.8Å. This corresponds to the more populuated split second neighbour silicon shell, as observed in the neodymium results. Successful modelling of the more minor component to this split silicon shell is not expected due to the markedly more dominant backscattering of the germanium atom in the vicinity of this silicon correlation. There are several possible origins of this structural difference between these two erbium samples: the slightly greater presence of germanium may be critical; the presence of the aluminium oxide may distort the environment such that the larger four-fold atom becomes more favourable near the rare-earth ion; the markedly differing concentration levels of the rare-earth ion may incur this effect; alternatively, the differences may result from a combination of several of these disparities.

EXAFS data of this sample were also collected as a function of radial distribution from the preform core. The results from the core centre and at 100 μm from the centre are similar. At 200 μm one can no longer suitably model the split oxygen shell and at 300 μm one can no longer model the silicon shell. Suitable models for the results at 400 μm and 500 μm have not been obtained. The origin of these differences is presently being resolved.

Attempts to model rare-earth - rare-earth correlations in results from all samples were unsuccesful, thus indicating a minimum clustering distance of approximately 4Å.

[1] Bowron et al, J. Mat. Sci. (1996) **31** 485-490.