ESRF	**Experiment title:** XAS measurements on silica xerogels doped with rare earth ions	**Experiment number:** HC511
Beamline: BM8	**Date of experiment:** from: 16-Jun-96 to: 22-Jun-96	**Date of report:** 26-Feb-97
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Report:

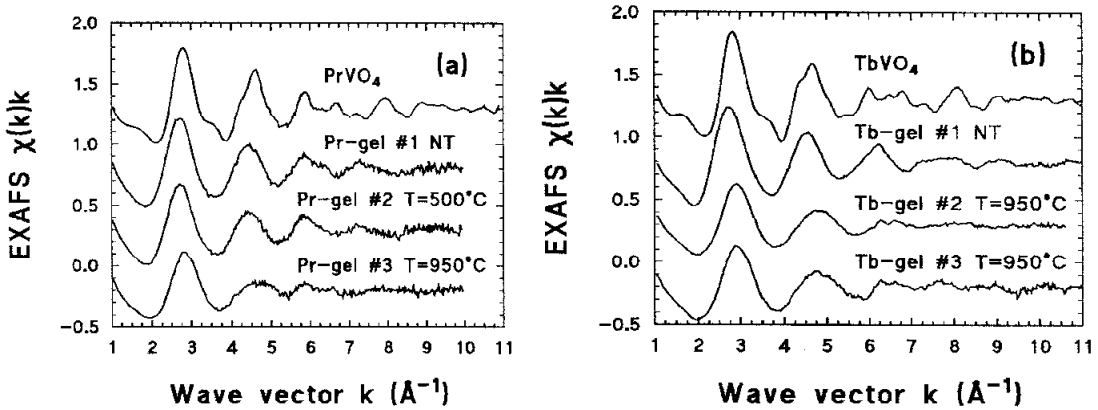
Rare earth doped silica xerogels are of great interest for technological applications in the field of optical devices. The operational properties of such devices are directly linked to the local atomic and electronic structure of the optically-active dopant ions.

A full understanding of the structural and dynamical modifications during the gel-to-glass and gel-to-ceramic transitions is important in order to improve the quality of the final material. In particular, the optical properties are strongly modified when crystallization of the silica network or ion clustering of rare-earth oxides occur: these processes depend on different independent parameters: ionic radius of the rare-earth ion, concentration of dopant, heat treatment procedure.

During the last years we have widely investigated silica xerogels by optical spectroscopy. The main aim of these first EXAFS measurements was to study the local environment of Pr and Tb ions in gels produced by us in Trento and already optically characterized.

Due to the low concentration of dopant ions, measurements were performed in the X-ray fluorescence configuration, by using two different detectors: PIN Silicon photodiode or high resolution Ge. Two days (6 shifts) have been devoted to the preliminary characterization of performance and optimal parameters for these detectors: for Pr-doped xerogels and glasses we used both detector; for Tb-doped xerogels (5000-10000 ppm) we

used the PIN diode, because of the high intensity of X-ray fluorescence and background.
One of the main problem for quantitative EXAFS analysis of rare-earth's (RE) environment is to have a good reference compound, with symmetric environment in the first coordination shell: since the RE_2O_3 compounds are not satisfying this condition, we have produced by solid state reaction PrV04 and TbV04 crystals: these reference crystals were measured in transmission configuration at room temperature and successfully utilized in optimizing the parameters for theoretical calculations of backscattering amplitude and phase shift functions.
Some experimental EXAFS signals are presented in the figure below: a) from top: PrVO4, Pr-doped xerogels with 10000 ppm not thermally treated (NT), and treated at 500 and 950 C; b) $TbVO_4$, Tb-doped xerogel with 10000 ppm NT, the same treated and 950 C, and with 5000 ppm treated at 950 C.



Due to the high distortion of the local environment of RE ions, the quantitative data analysis has been performed by using the software code EDA (developed by A. Kuzmin, Riga) which allows an ab initio reconstruction of the first-shell radial distribution function.
The main results can be summarized as follows: the local environment of Re ions in wet and densified silica xerogels is strongly modified by thermal treatment at temperature higher than 500 C; upon the densification process at 950 C the atoms within the first and second coordination shell around Pr and Tb ions relax, leading to a shortening of RE-0, RE-RE and RE-Si interatomic distances; and to a decrease of the coordination number within the first RE-0 coordination shell; the distortion of this shell is also increased during the densification process. This behavior seems to be quite general for RE ions in xerogels, but the quantitative analysis shows very different structural parameters for Pr and Tb ions. This fact can be explained in terms of different electropositivity and ionic size, and will be compared with the different optical properties of the obtained xerogels.
The local environment of Pr in zinc borate glasses has been also measured, because gels and glasses show very different optical properties. A summary of these first EXAFS results will be presented at the NCM7 Int. Conference (Cagliari, Italy, Sept. 1997).