ESRF	**Experiment title:** XAS measurements on silica xerogels doped with rare earth ions	**Experiment number:** CH-395
Beamline: BM08 GILDA	**Date of experiment:** from: 3 0-Aug-97 to: 02-Sep-97	**Date of report:** 27-Feb-98
Shifts:	**Local contact(s):**	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

- *ROCCA Francesco, *ARMELLINI Cristina, *DALMASO Alberto and FERRARI Maurizio
  CeFSA- Centro CNR-ITC di Fisica degli Stati Aggregati, 38050 POVO (Trento), Italy
- KUZMIN Alexei
  Institute of Solid State Physics, University of Latvia, LV- 1063 RIGA, Latvia
- *MONT1 Francesca
  Facolta'di Scienze Universita di Verona, Italy

Report:

Rare-earth doped silica xerogels are of great interest for technological applications in the field of optical devices, whose properties 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.

The present EXAFS project is part of a Research Program aimed at studying the local environment of rare-earth ions in a wide set of silica xerogels produced, heat treated and optically characterized in our Laboratory in Trento. We have already studied Pr^{3+} -doped gels and glasses (cf. ESRF Exp.Rep.:HC5 11) [1].

The local environment around terbium ions has been studied at BMOS-GILDA at the Tb L_3 and L_1 edges in Tb-doped silica xerogels (400 , 5000, 10000, 20000 and 40000 ppm Tb/Si) in fluorescence, and in some reference compounds: 0.02 and 0.1 M aqueous solutions of $Tb(NO_3)_3 \cdot 6H_2O$ salt, $BaTbO_3$, $BaBi_{0.2}Tb_{0.8}O_3$ and $TbV0_4$ in transmission.

The spectra of xerogels, $BaTbO_3$ and solutions were recorded at room temperature **(RT)** whereas that of $BaBi_{0.2}Tb_{0.8}O_3$ and $TbV0_4$ were also measured at 80 K and 180 K .
A large area PIN Silicon photodiode was used for fluorescent measurements, except for the 400 ppm Tb gels , where it was possible to use a 7-element Ge multidetector in a linear regime.

Preliminary results

The L_3 XANES in solutions, xerogels and $TbV0_4$ are similar, showing a sharp white line: this corresponds to Tb^{3}+ valence state; BaTbO, and $BaBi_{0.2}Tb_{0.8}O_3$ show a much complex behavior, due to a different coordination number (6 instead than 8) and to the presence of some Tb^{4+} ions in $BaBi_{0.2}Tb_{0.8}O_3$.

Both XANES and EXAFS regions of the x-ray absorption spectra were analyzed within the ab-initio multiple-scattering approach for all the reference compounds. For the analysis of xerogels, the experimental backscattering amplitude and phase shift signals obtained from the concentrated water solution were also used, with physical parameters obtained from the preliminary ab-initio study.

The EXAFS of Tb^{3+} in water solutions is well interpreted taking into account the MS effects within the first shell TbO_8 antiprism with R(Tb-O)=2.40 A.

The quantitative analysis of the radial distribution functions (Rdf) within the first coordination shell of terbium in as prepared (NT-) and heat treated at 950 C (T-) xerogels has been performed using three different approaches: a)cumulant analysis method, b) standard two-shell minimization and c) the model-independent Rdf reconstruction provided by EDA software (by A. Kuzmin): results confirm our previous conclusions on the densification process of rare-earths doped silica xerogels. The local environment of Tb^{3+} in NT-xerogels is similar to that in water solution, showing a gaussian Rdf, with slightly larger Tb-0 distances, 2.45 Å. The thermal treatment induces a decrease of interatomic distances (Δr = - 0.5 Å), accompanied by a big distortion of the Rdf. A shoulder at longer distances appears for all the T-xerogels, and progressively increases with Tb concentration. The coordination number in NT-xerogels is decreasing with concentration to a value about 5-6 for the 40000 ppm sample; the thermal treatment furtherly reduces the coordination number of about 20-25%.

A preliminary analysis has been performed also on the next nearest coordination shells: in NT-xerogels there is a strong contribution from about 4 (for 400 ppm), 12 (for 10000 ppm) and 13 (for 40000 ppm) Tb atoms at 3.95-4.00 Å plus about l-2 Si atoms at 3.74-3.82 A.; the contribution of the second shell becomes weaker for T-xerogels, suggesting a strong influence of the silica matrix densification on the disorder around Tb.

References

1 - **F.Rocca,** G.Dalba, R.Grisenti, M.Bettinelli, F.Monti and A.Kuzmin: “An EXAFS study of the local environment of Pr^{3+} ions in silica xerogels and zinc borate glasses”, J. Non-Crystalline Solids, (1998) in print