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Report:

Rare earth (RE) doped silica xerogels are of great interest for technological applications in the field of optical devices: their optical 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 and/or ion clustering of rare-earth oxides occur: these processes depend on different independent parameters, such as ionic radius of the rare-earth ion, concentration of dopant (and co-dopants), 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 at CNR-CeFsa, in Trento.

During the last years, silica xerogels doped with Pr^{3+}, Tb^{3+} and Er^{3+} in a wide range of concentration (from 400 to 40000 ppm RE/Si) were studied at GILDA by X-ray Absorption Spectroscopy, together with some crystalline and liquid reference compounds. Due to the low concentration of dopant ions, measurements were performed in the focusing configuration, with X-ray fluorescence detectors: a PIN Silicon photodiode or a high-resolution multielement Ge detector, depending on energy and photon intensity.

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 a water solution containing the RE-ions were also used, with physical parameters obtained from the preliminary ab-initio study.

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, Tb and Er ions relax,

leading to a shortening of RE-O and RE-Si interatomic distances and to a decrease of the coordination number within the first RE-O coordination shell. The Radial distribution functions (RDF) of the non-thermally treated gels are characterized by a nearly gaussian shape, as for the reference sample. On the contrary, the RFD's of the densified gels are asymmetric. This behavior seems to be quite general for RE ions in xerogels, but the quantitative analysis shows different structural parameters for different RE ions. This fact can be explained in terms of different electropositivity and ionic size and can be compared with the different optical properties of the obtained xerogels.

The accurate analysis of the next nearest shells around the RE ions allows us to exclude a significant presence of a RE-RE coordination, at least up to a distance of 4 Å. Even at the highest concentrations, EXAFS measurements exclude the nucleation of RE-rich ordered clusters: this means that the quenching of the luminescence attributed to clustering effects in the literature originates from interactions at longer range.

The main topic of the present experiment (HS-612) was the extension of previous studies to the local environment around Er^{3+} ions in silica xerogels co-doped with aluminium. In fact, alumina addition was found to improve the dispersion of the optically active ion in silica glasses prepared by sol-gel route.

The local environment around Er^{3+} ions in wet and densified at 900 C silica xerogels (pure and co-doped with aluminium) has been studied at the Er L_3-edge by x-ray absorption spectroscopy using the fluorescence detection technique in a wide range of Er concentration.

The radial distribution functions (RDF), reconstructed from EXAFS, show several changes in the local coordination of erbium ions upon densification: shortening of the Er-O and Er-Si/Al distances, decrease of the coordination numbers and broadening of the Er-O RDF.

The effect of Al co-doping is clearly monitored by EXAFS in both the first and second coordination shells for densified gels and mainly in the second shell for wet gels.

At increasing Al content, the interatomic distances between the erbium ions and the ions of the second coordination shell (Si or Al) become longer and have narrower distribution. A preferential bonding of Er to Al ions is clearly detected, with increasing ordering at higher Al content.

EXAFS does not show evidence of a clustering for Er^{3+} ions after densification: the short range Er-Er coordination is absent or not detectable in the present experiments.

These results suggest that aluminium ions are located in the neighborhood of erbium in both wet and densified xerogels: they are mainly distributed within the pores of silica gel, where the rare-earth ions enter. The preferential substitution of Si by Al atoms in the local environment of erbium is at the origin of the improvement of optical properties shown by Al co-doped silica gels.

Published Papers from Measurements at ESRF in this Project :

- F. Rocca, G. Dalba, R. Grisenti, M. Bettinelli, F. Monti and A. Kuzmin : *Extended x-ray absorption fine structure measurements of the local environment pf Pr^{3+} ions in silica xerogels and zinc borate glasses*, J. Non-Cryst. Solids 232-324, 581-586 (1998).
- F. Rocca, F. Monti, A. Kuzmin, A. Dalmaso and D. Pasqualini: *EXAFS study of Tb-doped silica xerogels*, J. Synchrotron Rad. 6, 737-739 (1999).
- F. Rocca, M. Ferrari, A. Kuzmin, N. Daldosso, C. Duverger and F. Monti: *EXAFS studies on the local structure of Er ions in Al-codoped silica xerogels*. Paper presented at the 8th Int. Conf. on the Structure of Non-Crystalline Materials (Aberystwith (UK), August 2000), to be published in J. Non-Crystalline solids.
- F. Rocca, F. Monti, A. Kuzmin and M. Ferrari: *Effect of densification on the local structure around Pr^{3+} and Tb^{3+} ions in silica xerogels: an x-ray absorption spectroscopy stydy*, J. Non-Cryst. Solids, (2000) submitted.