EXAFS study of Tb-doped silica xerogels

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The modification of the local environment of Tb^{3+} ions in optically active silica xerogels as a function of concentration (from 400 ppm to 40000 ppm) and thermal treatment (which induces densification) was studied by x-ray absorption spectroscopy at the Tb L_3 edge. Quantitative analysis of the first Tb-O coordination shell was performed using the experimental signal from Tb^{3+} ions in water solution as a reference. The radial distribution functions (RDF) of the non-thermally treated (NT) gels are characterised by a nearly gaussian shape, as for the reference sample. On the contrary, the RDF of the densified gels (T) are asymmetric having the main peak at a shorter distance, with a reduced coordination number (N=4-5) and a secondary peak, with N=1-2, at a longer distance. The local environment of Tb in the low concentration sample (400 ppm) is different from that at higher concentrations, both in the NT- and in the T-gels.

1. Introduction

Silica xerogels activated by rare-earth (RE) doping ions are of great interest for their possible applications in photonics and optoelectronics (mainly in the field of telecommunications).

The optical properties of these systems are strongly dependent on the local structure around the active RE ions and on their relative distribution in the host glassy matrix. The quenching of the optical activity is currently attributed to different causes, the most important being the effect of phonon relaxation processes (mainly related to the coupling with the vibrations of the oxygen atoms surrounding the RE ions) and the effect of non radiative energy transfer between "near" RE ions (in many cases, the higher the RE concentration, the lower their optical activity) (Bouajaj *et al.*, 1995).

EXAFS studies can provide very accurate information on the short range environment of RE ions; however, some experimental conditions limit the potentialities of this technique: a) the L-edge studies allow to collect data only in a reduced energy range (losing R-space resolution) while, in the K-edge studies, core-hole life-time and photon statistics shorten the *R*-range practically only to the first coordination shell; b) the low concentration of RE ions requires the use of x-ray fluorescence detection and of high intensity focusing beamlines, only recently available at 3rd generation synchrotron radiation facilities.

The main aim of this paper is to present a study on the modifications of the first coordination shell of Tb^{3+} ions in silica xerogels as a function of concentration and densification. In

particular, we are interested in characterising the strong distortion produced during the final process of the xerogels preparation: the long time high temperature treatment, in fact, results in an overall relaxation of the silica network and in the elimination of the wet components, from precursor materials, present in the pores of the gels at the first stage of preparation (Rocca *et al.*, 1998).

2. Experimental

Transparent, monolithic samples of silica xerogels with different Tb concentration (from 400 up to 40000 ppm) were produced via standard hydrolysis and slow condensation at 60 °C (NT samples) (Bouajai *et al.*, 1997). Some of the NT xerogels were successively densified via thermal treatment at 950 °C for 120 hours (T samples) (Pucker *et al.*, 1998). A diluted (0.1 M) solution of $Tb(NO_3)_3$ in bidistilled water was prepared as reference compound.

The Tb L_3-edge x-ray absorption spectra were recorded at ESRF (Grenoble - France) at the BM8-GILDA beamline, using the Si(311) sagittally curved monochromator (Pascarelli *et al.*, 1996). Thanks to the focusing properties of the beamline, a fixed beam spot size of about 4 mm^2 was obtained. The x-ray fluorescence signal was collected by using a 7-element Ge solid state detector for the 400 ppm samples and a Si-PIN detector for the higher concentration ones (Dalba *et al.*, 1996). The reference compound was measured in standard transmission configuration.

3. Data analysis and results

The experimental EXAFS signals were extracted following a standard procedure (Dalba *et al.*, 1993; Kuzmin *et al.*, 1996).
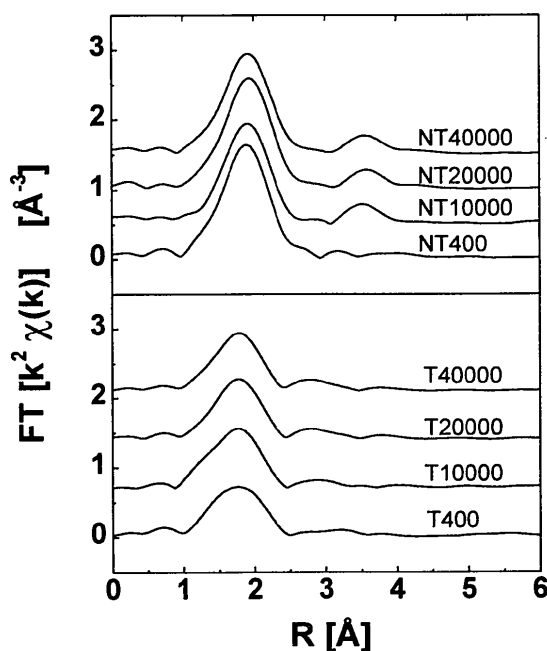

Figure 1
k^2-weighted Fourier transform of the Tb-doped silica gels as prepared (top) and after the densification process (bottom). The numbers indicate the Tb concentration in ppm.

The energy origin of the photoelectron E_0 = 7514 eV was determined by aligning the experimental EXAFS signal with that calculated for the reference solution. The EXAFS calculations for Tb in aqueous solution were performed using the FEFF6 code (Zabinsky et al., 1995) for a TbO_8 cube antiprism with R(Tb-O) = 2.40 Å.

As it can be seen in the Fourier Transforms shown in Fig. 1, the temperature treatment strongly modifies the local environment around Tb ions; moreover, both in the NT and in the T gels, clear differences are visible in the first as well as in the second coordination shell between the low concentration sample at 400 ppm and the higher concentration ones.

The data analysis of the first Tb-O coordination shell was performed using two very different approaches, in order to have more elements to assess the reliability of obtained results. The first approach uses the EXTRA software package, developed at University of Trento (Dalba et al., 1993); the second one uses the EDA software package, developed at Institute of Solid State Physics, Riga (Kuzmin et al., 1996; Kuzmin, 1997). EXTRA allows a fast graphic recognition of asymmetry or anharmonicity by plotting and best-fitting the amplitude ratio and the phase-shift difference with even and odd cumulants independently (Dalba & Fornasini, 1997). EDA is able to reconstruct a model independent radial distribution function (RDF), by a regularization procedure performed in the k-space: this method is very useful when the cumulant expansion diverges and whenever many distances are present under the same FT peak.

Experimental phase-shift and amplitude functions for the Tb-O distances were extracted within the gaussian approximation from the first shell EXAFS signal of Tb in aqueous solution, using two different Fourier Transform windows (in the range 1-11.92 Å^{-1} with a gaussian window and in the range 0.1-13.5 Å^{-1} with a Kaiser-Bessel window) and backtransforming in the range 0.8-2.82 Å: the experimental functions obtained in the two cases by setting R=2.40 Å, N=8 and σ^2=0.01 Å^2 (Yamaguchi et al., 1988) are identical and agree with our calculations by the FEFF6 code in the k range 2.5-9 Å^{-1}.

Since EXTRA and EDA contain different windowing functions for the FT, slightly different FT ranges were chosen for the experimental EXAFS signals $k^2\chi(k)$ of Tb doped gels: 2.65-9 Å^{-1} using a gaussian window in EXTRA; 1-9 Å^{-1} using a gaussian window and 1-10.5 Å^{-1} using a Kaiser-Bessel window in EDA. The contribution to the EXAFS signal from the first coordination shell was singled out by back-FT in the range 0.9-2.6 Å. The quantitative analysis by EXTRA and EDA was performed in slightly shortened k- ranges, chosen to reduce the influence of noise present in the experimental data at high k values.

3.1 EXTRA results

The phase-shift difference and the logarithm of amplitude ratio were best fitted for all the samples in the k range 3-7 Å^{-1}. The results obtained indicate that for all the NT gels the RDF is practically gaussian, with a negligible value of the third cumulant C_3; the Tb-O distance is shifted on average of about +0.04 Å with respect to the reference solution ($<R>$ = 2.44 Å); the behaviour of the low concentration sample (400 ppm) is different from the high concentration ones: in the NT 400 ppm gel, the coordination number, N, is about 8 and σ^2 is slightly greater of about +0.003 Å^2 than the solution, while at the high concentrations N is about 6 and σ^2 is slightly lower of about 0.001-0.002 Å^2 than the solution.
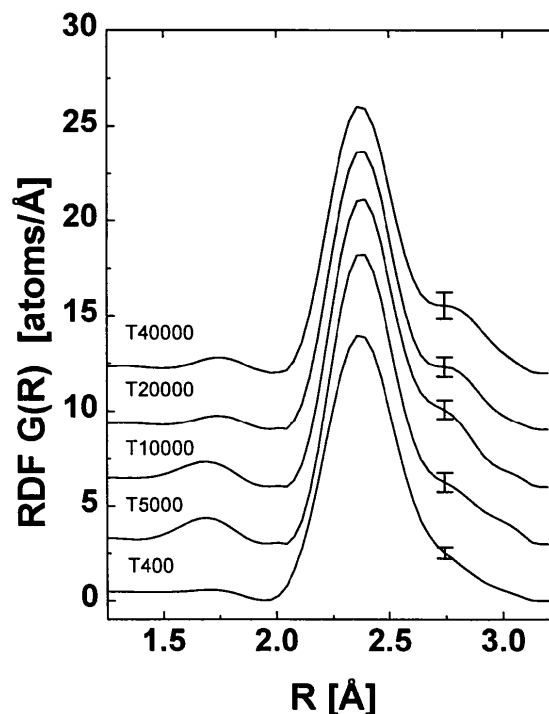

Figure 2
Radial distribution functions obtained by EDA software for the T gels, densified with a thermal treatment of 120 hours at 950 °C.

The analysis of the T gels indicates the presence of an asymmetry in the distribution, shown by strong deviations of the phase-shifts and amplitude functions mainly at k values higher than 7 Å^{-1}.

A quantitative analysis gives C_3 values greater than 10^{-3} Å^3, and average distances ($<R>$ = 2.37 Å) reduced of about -0.03 Å with respect to the reference solution; the behaviour of the low concentration sample is again different from the high concentration ones: in the T 400 ppm gel the amplitude ratio analysis (limited to the 4th cumulant C_4) gives N about 5 and σ^2 greater of about +0.008 Å^2 than in the solution, while at the high concentrations N results about 4 and σ^2 is comparable to the solution. We will discuss later the meaning of these values.

3.2 EDA results

The first shell EXAFS signals of the NT gels were successfully best fitted in the k-space over the range 2.65-9 Å^{-1} using a simple one-gaussian function, as suggested by the ratio-method results. The corresponding values of coordination numbers, mean distances and Debye-Waller factors are in good agreement with the results obtained by the ratio-method using EXTRA. The best-fit using two-gaussian functions did not improve the results significantly.

The case of the T gels, where the ratio-method analysis indicates a high degree of disorder, is quite different: the one-gaussian model is not able to reproduce the EXAFS signal. We obtained reliable results using the ab initio RDF reconstruction procedure (Kuzmin et al., 1996; Kuzmin, 1997): the best fit in the k-space was performed over the range 2.65-7 Å^{-1}, starting from different

input values to test for convergence and reproducibility. The reconstructed RDFs are presented in Fig. 2: they show an asymmetric distribution of the Tb-O distances, with a tail on the long distance side. The error bars in the figure indicate the range of the different values obtained at each point of the reconstructed RDFs: they take into account the effect of different EXAFS extraction and best fitting parameters.

In order to obtain quantitative results, the obtained RDFs were successively best fitted by two gaussian functions. The main peak is centred for all the T gels about 2.37 Å, with N=4-5; the secondary peak, which is higher at increasing Tb content, has N=1-2. The behaviour of the low concentration sample is different from that of the high concentration ones also in the T gels: the Debye-Waller factor σ^2 of the main peak is higher in the T400 sample than in the high concentration ones, while the secondary peak shifts from 2.70 Å towards higher distances (2.74-2.76 Å) in the high concentration samples, where it is better resolved.

4. Discussion

The comparison between the results obtained by EXTRA and EDA analyses allows to describe the local environment of Tb ions in these silica xerogels, in particular the changes produced during the final process at high temperature, which is the most important step to obtain transparent gels suitable for optical applications.

Before densification, all the obtained parameters indicate that Tb ions are in a liquid-like environment, with a gaussian distribution of Tb-O distances. The preferred coordination is with the oxygen atoms of the hydroxyl and ethoxyl groups contained in the pores of the silica gels (Campostrini *et al.*, 1992). The NT 400 ppm gel shows an RDF which is more similar to the reference solution, while at increasing concentrations a significant reduction of the coordination number (not accompanied by a shortening of the average distance) and a slight decrease of the Debye-Waller factor are clearly evidenced by the two analyses. The FTs presented in Fig. 1 (top) confirm this difference, because a contribution centred at about 3.6 Å is present in the high concentration samples. At this stage of the analysis, the origin of this feature is not clear: since it disappears for the densified gels (Fig. 1, bottom), we can suppose that a direct Tb-Tb correlation is not present. This peak might originate from multiple scattering paths in the first coordination shell or from a more defined coordination with Si atoms of the silica host. Future studies will try to clarify this point.

As for the densified gels, at first we can note that both EXTRA and EDA analysis agree in the indication of a shortening of the Tb-O mean distance and in a general reduction of the coordination number. The cumulant analysis (EXTRA), however, seems to be sensitive only to the main peak parameters. The presence of a Tb-O coordination at higher distances in the first coordination shell is very well shown by the RDFs obtained by EDA and is the main cause of the non-convergence of the cumulant expansion.

The shortening of the main Tb-O distance is related to the relaxation produced to the silica chains by the thermal treatment. Since the wet components from precursors are eliminated, Tb ions are now directly coordinated to the oxygens of the SiO_2 network, at a distance which is not very much influenced by the Tb concentration. We note that the most disordered environment is shown by the T400 gel, while the higher concentrations are

characterised by lower coordination numbers and Debye-Waller factors. This "ordering" is accompanied by the growing importance of the longer Tb-O coordination. We can explain these results with an active role during the densification process of Tb ions, which are locally modifying the network around them, in order to maintain the preferred Tb-O distances. Our EXAFS measurements do not show significative differences when the Tb content is increased from 5000 to 40000 ppm: this is a further confirmation that the local structure around Tb in the densified silica gels is mainly influenced by the very short range coordinations.

The densified gels, moreover, do not present evidence of ordered Tb-Tb correlations: this implies that even at the higher concentrations, where a luminescence quenching is observed (Pucker *et al.*, 1998), we can exclude the nucleation of Tb-rich ordered clusters, in agreement with similar measurements on Pr-doped silica gels and glasses (Rocca *et al.*, 1998; Braglia *et al.*, 1998). The Tb-Tb distance is expected at about 3.8 Å from x-ray diffraction measurements (Rocca & Dalmaso, 1998): its contribution to the EXAFS signal, however, is very low due to a high static disorder. The low peak in the FT centred at about 3 Å in the T gels (Fig. 1, bottom) can contain both Tb-Si and Tb-Tb distances: it will be analysed in the future in parallel with the analysis of x-ray diffraction measurements.

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