Short-range order around Er\(^{3+}\) in silica waveguides containing aluminium, titanium and hafnium

N.D. Afify a, R. Grisenti a, G. Dalba a, C. Armellini b, M. Ferrari b, S. Larcheri b, F. Rocca b,*, A. Kuzmin c

a INFM and Department of Physics, 38050 Povo, Trento, Italy
b IFN-CNR, Institute for Photonics and Nanotechnologies, Section ‘ITC-CeFSA’ of Trento, 38050 Povo, Trento, Italy
c Institute of Solid State Physics, University of Latvia, LV-1063 Riga, Latvia

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Abstract

Er\(^{3+}\)-doped silica waveguides, co-doped with aluminium, titanium, and hafnium oxides, were prepared using the sol–gel method and dip-coating processing. Here, we present a characterisation of the local environment around Er\(^{3+}\) ions, as determined from the Er L\(_3\)-edge extended X-ray absorption fine structure (EXAFS) measurements performed at ESRF (France). The first coordination shell is composed of 5–6 oxygen atoms at distances \(\approx 2.32–2.35\) Å, slightly varying as a function of the modifier oxide. Er\(^{3+}\) nearest neighbors distance does not show a significant compositional dependence. On the contrary, outer shells analysis shows significant differences: Al\(_2\)O\(_3\) doping (less than 2% mol) induces an ordering around Er and increases the distance of the second shell, probably due to the substitution of Si by Al atoms; for TiO\(_2\) doping (7–15% mol), it is most probable that the second shell is composed from Si atoms as the case of pure SiO\(_2\); for HfO\(_2\) doping (from 10 to 50 mol%) there is a very clear evidence of Er–Hf coordination already at the lowest Hf content, but still in amorphous environment.

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1. Introduction

Among the different technologies which are employed to develop materials suitable for photonics, sol–gel processing exhibits several advantages in terms of rare-earth solubility, composition, design, tailoring of optical properties as well as fabrication of films, waveguides, photonic crystals, and bulk glasses. The binary silica-based systems, such as silica–titania, silica–hafnia, and silica–alumina, are of particular interest allowing the tailoring of the optical and spectroscopic properties [1]. Information on the nearest and next-nearest coordination shells of the rare-earth ions in the glass host is of crucial importance to design and select the system with optimised spectral properties for fabricating active devices such as planar optical amplifiers.

For this purpose, we present here a comparison between the local structure around Er\(^{3+}\) ions in silica glass co-doped with different modifier oxides. In previous publications we presented the local structure around Er\(^{3+}\) ions in pure SiO\(_2\) and SiO\(_2\)–Al\(_2\)O\(_3\) networks [2,3]. We showed that co-doping of SiO\(_2\) with few mol% of Al was sufficient to induce significant changes beyond the first coordination shell. Here we report on new EXAFS experiments on SiO\(_2\)–TiO\(_2\) and SiO\(_2\)–HfO\(_2\) waveguides. In the last system, in particular, spectroscopic studies have shown a strong modification of the crystal field strength around the Er\(^{3+}\) ion, leading to an increase of the electric dipole component of the \(4I_{13/2} \rightarrow 4I_{15/2}\) transition probability [4,5].

2. Experimental and data analysis method

Er\(^{3+}\)-doped SiO\(_2\)–TiO\(_2\) and SiO\(_2\)–HfO\(_2\) solutions with different modifier contents (7, 12, and 15 mol% for TiO\(_2\); 10, 20, 30, 40, and 50 mol% for HfO\(_2\)) were prepared using
the sol–gel method and deposited on v-SiO₂ substrates using the dip-coating processing [4]. Composition and thermal history of different samples are compiled in Table 1.

X-ray absorption measurements were performed at room temperature (RT) in fluorescence mode at the Er L₃-edge using synchrotron radiation at the BM08 GILDA CRG beamline of ESRF (Grenoble, France) [2,3]. 0.1 M aqueous solution of Er(NO₃)₃·5H₂O salt, crystalline ErVO₄ and Er₂O₃ powders were also measured in transmission mode as reference compounds. EXAFS data were analysed using the EDA code [6] as described in [6,7]. To model the different EXAFS spectra, we followed the usual Gaussian multi-shell fitting procedure, using either theoretical or experimental backscattering amplitudes and phase shifts. The theoretical ones were calculated using the FEFF8 code [8] and optimized to reproduce the experimental EXAFS signals of the measured reference compounds.

![Fig. 1](image)

Fig. 1. Experimental (dotted lines) and calculated (solid lines) Fourier transforms of the Er L₃-edge EXAFS signals $k^2 \chi(k)$ with different modifier oxides. Spectra from different systems were vertically shifted for clarity. See text for details.

The first coordination shell around Er³⁺, for all the samples under study, is composed of oxygen atoms; this shell was evaluated using experimental and theoretical backscattering amplitudes and phase shifts extracted from different sources. As experimental scattering functions, we used those extracted from EXAFS spectra at the Er L₃-edge for Er nitrate hydrate water solution, while the theoretical ones were calculated starting from the structure of polycrystalline Er₂O₃. It is worth mentioning here that in previous publications on similar systems, the first shell distances evaluated by us were significantly larger than those reported by D’Acapito et al. [9,10]. In order to verify if such differences were due to our analysis procedures, we have checked the reliability of our results by varying the fitting strategies, scattering functions and so on. In all cases we got values that agree with each other within 0.01 Å as an overall error bar, and our previous results were confirmed [2,3]. The obtained structural parameters relative to the first coordination shell are compiled in Table 1.

For the second coordination shell, the backscattering amplitudes and phase shifts for Er–Si, Er–Al, Er–Ti, and Er–Hf atomic pairs were calculated starting from the structure of crystalline ErVO₄ by replacing V by Si, Al, Ti and Hf respectively. For each sample, all the possible next-coordination shells were considered, and their structural parameters are compiled in Table 1.
nearest shell correlations were tested and the plausible solutions were then evaluated. The possibility of the presence of Er → Er coordination was also tried. For all samples, the fit ruled out such correlation at the very beginning, confirming the results of previous EXAFS studies [2,3,9,10].

The structural parameters for the second coordination shell are reported in Table 1, while some examples of the fit are shown in Fig. 1.

As it might be seen from Fig. 1, the quality of best fit is very high, but we should note that the quantitative determination of the outer shells content was in some cases ambiguous. A first reason is due to the fact that the contributions of these shells to the experimental spectra are smeared out by the structural disorder and hence only a short $k$ range of the spectra can be reliably fitted. Another reason is the impossibility to distinguish between the backscattering functions of Al, Si and the high similarity in case of Ti atoms. The most favorable case is that of SiO$_2$–HfO$_2$ system, because the backscattering amplitude of hafnium is double-peaked and clearly identifiable.

3. Results and discussion

Let us first discuss the results relative to the first coordination shell of Er$^{3+}$ in the different oxide matrices. From the experimental and calculated Fourier transforms reported in Fig. 1, and the structural parameters compiled in Table 1, the first coordination shell in all the investigated samples is composed of 5–6 oxygen atoms at distances $\pm 2.32–2.35$ Å. The first coordination shell is not influenced significantly neither by varying the network modifier nor its concentration. This can be seen as a general trend of Er$^{3+}$-doped silica glass co-doped with different network modifiers, in case of thermal treatments performed at the same temperature.

The situation in the case of outer coordination shells is much more different and complicated from the first one. The content of the outer shell depends, to a large extent, on type and content of the modifier oxide. The case of pure SiO$_2$ is the simplest one. Er$^{3+}$ in this case is coordinated only by silicon atoms and the EXAFS signal was best fitted on the basis of a single Er–Si shell centered at $\pm 3.74$ Å. The effect of co-doping SiO$_2$ with Al$_2$O$_3$ is documented in Fig. 1: even though the low molar content, the presence of Al atoms leads to considerable changes beyond the first shell. The quantitative analysis shows a clear evidence of the presence of hafnium in the second shell, that can be very well fitted by a single distance. The comparison with may explain the improvement of optical properties shown by Al co-doped silica gels [12,13].

The identification of the outer shell in the case of SiO$_2$–TiO$_2$ was much more complicated, because a single Er$^{3+}$–Si or Er$^{3+}$–Ti distance was not able to reproduce the frequencies of the next-nearest shells. Moreover, a distinction between silicon and titanium atoms was impossible on the basis of a multi-shell best fit. We have thus followed an alternative procedure: as a first step, the contribution of the Er$^{3+}$–O first coordination shell has been evaluated and then subtracted from the whole EXAFS spectrum. The residual was then filtered from noise and reasonable data ranges were estimated for best fitting the outer shells. In this case, only two silicon distances could reproduce, almost perfectly, the residual signal beyond the first shell as shown in Fig. 2. This implies that Er$^{3+}$ is coordinated by silicon atoms as second nearest neighbors. This assumption is supported by the well known fact that in SiO$_2$–TiO$_2$, TiO$_2$ has a known tendency to be phase separated or assume a random-like nature [11]. No detectable effect on the second shell was present by varying TiO$_2$ content as reported in Table 1.

For co-doping with HfO$_2$, we have investigated a wide range of composition, on samples where XRD did not show any evidence of nucleation or crystallization. The next-nearest shells are strongly modified by the presence of Hf. The quantitative analysis shows a clear evidence of the presence of hafnium in the second shell, that can be very well fitted by a single distance. The comparison with

![Fig. 2. Fitting of the residual signals corresponding to next-neighbor shells to four models of two distances (experimental (dotted lines) and calculated (solid lines)) as reported for 1% Er$^{3+}$-doped SiO$_2$:TiO$_2$ with 15% TiO$_2$ as an example.](image-url)
Al or Ti co-doped samples in Table 1 shows that the Er–Hf distance in the second shell is the shortest one, indicating a densification around Er. EXAFS results indicate that the co-doping with HfO2 induces a strong modification of the local environment of Er. However, within the explored compositional range, the obtained structural parameters for the second coordination shell remain constant, indicating the presence of HfO2-rich amorphous regions already at 10 mol% content. The present EXAFS results confirm the conclusions of Ref. [5], where the disruption role of hafnia on the silica network was supposed to be effective even at low HfO2 content. Photoluminescence spectra and lifetimes can be explained by considering that the incorporation of HfO2 in silica strongly modifies the next-nearest shell environment around Er3+, inducing an increase of the electric dipole component of the $^4$I$_{13/2}$–$^4$I$_{15/2}$ transition probability.

4. Conclusions

The first coordination shell around erbium in Er3+-doped SiO2 co-doped with different modifier oxides is composed from 5 to 6 oxygen atoms at distance ~2.32–2.35 Å. This shell is not influenced, significantly, neither by varying the type nor the content of the network modifier.

The situation for the outer coordination shell is very different. The presence of titanium is not detectable in the local environment of erbium. The main effect of co-doping with a low molar content of aluminium is to hamper the clustering of erbium ions, due to the concentration of Al around Er. In the case of SiO2 co-doped with HfO2, Er3+ ions are mainly dispersed in an amorphous HfO2 environment, thus explaining why the optical properties are strongly modified with respect to the pure silica wave-guides.

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