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Relationship between structure and optical properties in rare earth-doped hafnium and silicon oxides: Modeling and spectroscopic measurements

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ABSTRACT

The SiO₂–HfO₂ binary system is recognized as a promising candidate for Erbium-doped waveguides amplifiers fabrication. Recently, it was demonstrated that Er³⁺-activated 70SiO₂–30HfO₂ planar waveguides with valuable optical and structural properties can be prepared by sol-gel technique with dip-coating processing. The important role played by hafnium in the silica network was evidenced by the particular spectroscopic properties presented by Er³⁺-ions in the silica-hafnia planar waveguides. In this work we present preliminary results on HfO₂–SiO₂ bulk xerogels doped with Eu³⁺ ions, with the aim to go inside the role of hafnium on the rare earth ions local environment. Spectroscopic measurements of the Eu³⁺ photoluminescence emission are given. Numerical simulations by the molecular dynamics method have been performed showing clearly a phase separation for the HfO₂ richer samples. Moreover it is found that the rare earth-doping ions stay preferentially in hafnium rich domains, thus explaining why the rare earth spectroscopic properties are strongly modified.

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1. Introduction

During the last years, the impact of integrated optical devices for telecommunication technology is increasing. In particular, rare earth-doped planar waveguides have received a great interest due to their low cost and reduced size. Among several silica-based glasses it was demonstrated that the SiO₂–HfO₂ binary system is promising for successful applications in photonics [1]. According to the literature [2], phase separation in SiO₂–HfO₂ may occur depending on the HfO₂ concentration and the annealing temperature. Depending also on the thermal treatment, transparent glass ceramics based on the same system could be synthesized with the best properties for rare earth emission [3].

In this work, the relationship between the structure and the spectroscopic properties of Eu³⁺-doped SiO₂–HfO₂ systems is investigated by experimental photoluminescence measurements and by molecular dynamics modeling.

2. Experimental

A laboratory glass has been prepared using the sol-gel route (for details see Ref. [4]). Its composition was Hf/Si = 10/90 with Eu/(Hf+Si): 1 mol%. The sample was densified at the temperature of 900 °C for 300 h.

The Eu³⁺ photoluminescence spectrum is plotted in Fig 1. It is composed of several multiplet transitions ⁵D₀ → ⁷F_{J=0,1,...,6}. The first transition, ⁵D₀ → ⁷F₀, is spin-forbidden but allowed by *J*-mixing effects. Its intensity, position and shape are very sensitive to the electrostatic field due to the local structure and hence to the degree of covalence of the oxygen bonds [5]. The second transition, ⁵D₀ → ⁷F₁, is mainly magnetic dipolar and intensity-insensitive to the local field. However, its splitting feature is directly proportional to the crystal field strength. Comparisons between spectra obtained for a non-annealed sample, for a 900 °C heat-treated sample and for an alumina-silica glass [4] show dramatic changes due to the cationic second shell influence (Hf or Al). Costa et al. have attributed these effects to the codopant field strength (Z/r^2 ; *Z* = ionic charge, *r* = ionic radius of the cation) [6]. The stronger is this field, the more covalent is the rare earth (RE) environment and the weaker is the crystal field experienced by the RE ions. Following this proposition

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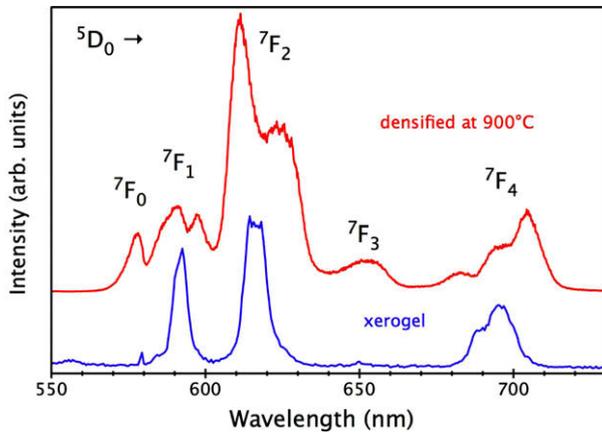


Fig. 1. Photoluminescence spectra recorded at room temperature for a Eu^{3+} -doped HfO_2 - SiO_2 xerogel and for the same sample densified at 900 °C.

and according to the codopant field strength, Hf^{4+} (7.94 \AA^{-2}) can be classified between Ga^{3+} (7.80 \AA^{-2}) and Al^{3+} (10.68 \AA^{-2}). In the case of disordered materials like glasses, an important inhomogeneous broadening of the emission bands occurs. This broadening is due to a continuous set of varying environments or sites experienced by the activator ion (Eu^{3+}). It has been shown that this broadening cannot be resolved by fluorescence line narrowing (FLN) experiments in pure silica glasses [5,6]. The common interpretation is that RE clustering favors the energy transfer, which prevents the site selection. In the meantime, incorporation of modifier ions like Al^{3+} would play an anti-clustering role and would lead to an increase of both the quantum efficiency and the site selection ability. Fig. 2 shows the FLN measurements performed on the hafnium codoped sample. It appears that site selection is possible as already claimed for the other modifier cations: the energy splitting i.e.,

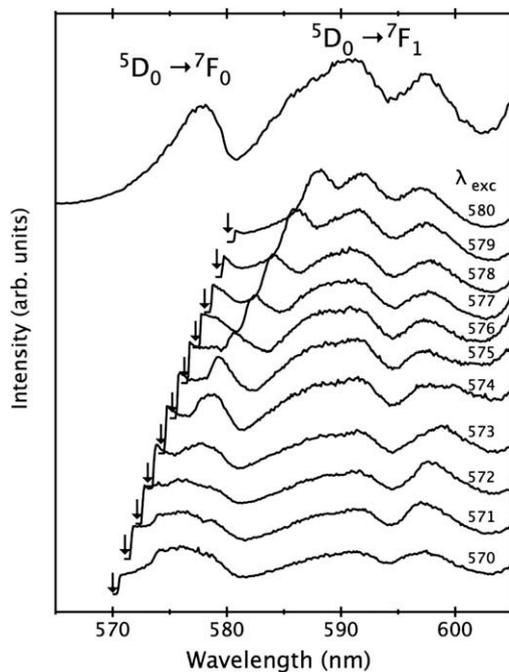


Fig. 2. Fluorescence line narrowing spectra to the 7F_1 Stark levels exciting selectively the electronic transition to the 5D_0 level in a Eu^{3+} -doped HfO_2 - SiO_2 glass at 77 K. Excitation wavelength is indicated for each spectrum (in nm) and with vertical arrows. The upper spectrum is the broadband emission to the $^7F_{0,1}$ levels obtained by exciting the 5L levels.

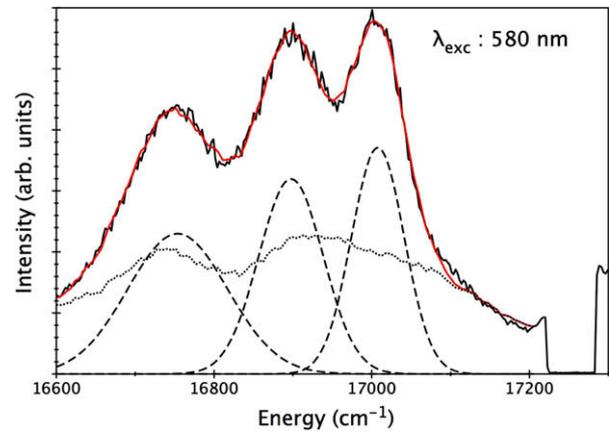


Fig. 3. Example of a fit for FLN spectra of the 7F_1 Stark levels with excitation at 580 nm. The experimental and fitted spectra are in continuous line. Dotted line represents the contribution of the broadband emission (see Fig. 2) and dashed Gaussian lines those of individual components.

the crystal field strength, increases with the excitation energy. In order to measure the positions of the energy components, we have fitted the FLN spectra with a combination of three narrowed lines and a residual broadband spectrum, according to the suggestion of Lavin et al. [7] (Fig. 3). The residual broadband spectrum comes from unperturbed sites by the codoping ions, and is similar to the spectrum recorded on non codoped samples. The superposition of both narrowed lines and broadband spectra can be interpreted as the co-existence of two kind of Eu sites: one highly influenced by the presence of hafnium, and the other one unperturbed. From the energy positions of the three Stark components of the $^5D_0 \rightarrow ^7F_1$ transition, we have calculated the second order crystal field parameters B_{20} and B_{22} . A second order crystal field strength $N_V(B_{2q})$ is then derived [8,9]. The second rank crystal field Hamiltonian is given by $H_{\text{CF}} = B_{20}C_0^{(2)} + B_{22}(C_{-2}^{(2)} + C_2^{(2)})$ where $C_q^{(2)}$ are Racah

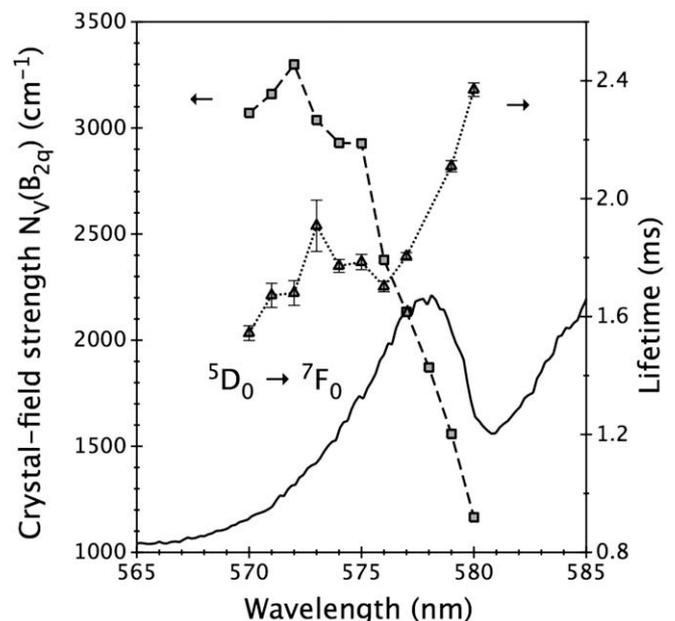


Fig. 4. Crystal field strength parameter (dash) and lifetime (dot) of the longest component into $^5D_0 \rightarrow ^7F_2$ decays as a function of the excitation wavelength within the $^7F_0 \rightarrow ^5D_0$ band. The $^5D_0 \rightarrow ^7F_0$ spectrum (continuous line) has been superposed in the figure.

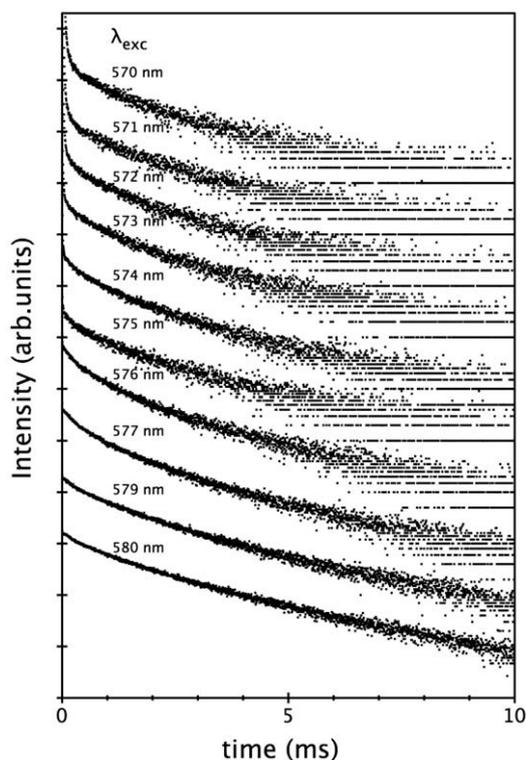


Fig. 5. Decay curves of the ${}^5D_0 \rightarrow {}^7F_2$ emission for different excitation wavelengths in a Eu^{3+} -doped $\text{HfO}_2\text{-SiO}_2$ glass at 77 K.

operators. Energy positions are related to the B_{kq} by the following equations:

$$E_1 = E_b + \frac{1}{5} B_{20}$$

$$E_2 = E_b - \frac{1}{10} B_{20} + \frac{\sqrt{6}}{10} B_{22}$$

$$E_3 = E_b - \frac{1}{10} B_{20} - \frac{\sqrt{6}}{10} B_{22}$$

where E_b is the barycentre of the ${}^5D_0 \rightarrow {}^7F_1$ multiplet. Then, the second order crystal field strength is given by: $N_v(B_{2q}) = \sqrt{\frac{4\pi}{5} (B_{20}^2 + 2B_{22}^2)}$. Values are reported in Fig. 4 together with the resonant emission line ${}^5D_0 \rightarrow {}^7F_0$ where the excitation was applied. The values of the long component decay time for the maximum

Table 1

Coordination number for the second coordination shell of silicon and hafnium

Hf/(Hf + Si) (%)	Si-Si at 3.4 Å	Si-Hf at 4 Å	Hf-Hf at 4.3 Å	Hf-Si at 4 Å
10	4.25	0.60	3.05	0.06
50	4.39	0.21	4.88	0.21
90	3.22	0.12	6.29	1.04

peak emission ${}^5D_0 \rightarrow {}^7F_2$ are also reported in Fig. 4. The decay curves are not exponential (Fig. 5) due to the residual inhomogeneous character of the emission. According to the excitation energy, two regimes appear clearly in Fig. 4. For the high energy wing, the crystal field strength is high and the decay time is short: both change a little; for the low energy wing, they both vary abruptly with the excitation energy: the crystal field strength decreases and the decay time increases. The introduction of Hf in the glass allows site selection experiments, especially in the red wing of the band. From the experiments, we get a continuous variation of the crystal field in opposition with what we get for the non codoped samples. These results lead us to conclude that most of the sites perturbed by the presence of Hf are located on the red wing of the ${}^5D_0 \rightarrow {}^7F_0$ band. The energy of this transition directly depends on the covalency of the Eu^{3+} bonding i.e., the so-called nephelauxetic effect [10]. The lowest energies correspond to the more covalent bonding environments. Thus, Hf-perturbed Eu^{3+} sites exhibit a more covalent character, which is due to: stronger field strength for Hf, weaker crystal-field strength for Eu and an oxygen-richer environment.

3. Simulations

Using the molecular dynamics (MD) numerical technique we have simulated two sets of Eu^{3+} doped $\text{SiO}_2\text{-HfO}_2$ samples of various compositions. $y \text{Eu}_2\text{O}_3 \cdot x \text{HfO}_2 \cdot (2048 - y - x) \text{SiO}_2$ with x corresponding to the ratio $\text{Hf}/(\text{Si} + \text{Hf}) = 5\%, 10\%, 20\%, 30\%, 40\%, 50\%, 60\%, 70\%, 80\%, 90\%$ and y corresponding to the concentration in europium of 2.4 and 4.9 mol%. Potentials and parameters can be found in Ref. [4], except for Hf for which we have used values given by Balducci et al. [11]. The usual processes of heating and cooling have been used (see Refs. [4,12]) in order to achieve a perfect disordered and mixed system. However, in difference with the previously studied silicates, it appears that the final structure shows a phase separation between Si-rich domains and Hf-rich domains (see Table 1). Even for a low silicon concentration, the second coordination shell of Si is mainly constituted of Si and for a low concentration of Hf, the second coordination shell of Hf is mainly constituted of Hf. Starting from a perfect mixed phase, this separation occurs at the melting temperature since the number of

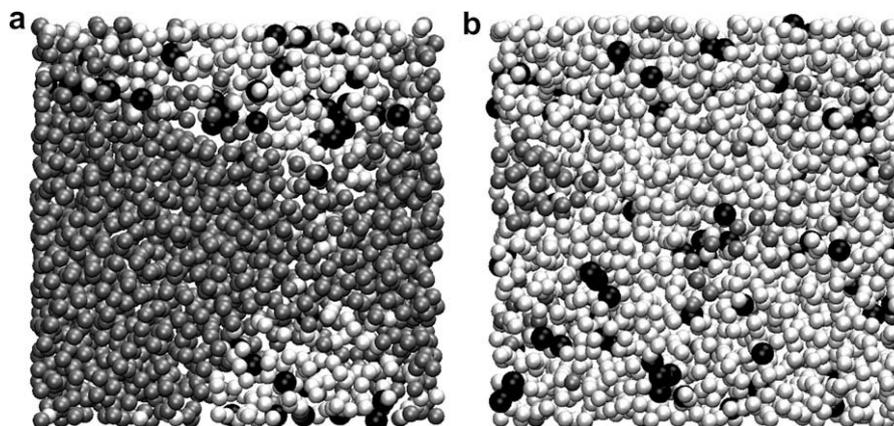


Fig. 6. Snapshots of two different samples. Small grey atoms are silicon, small white ones are hafnium and large black atoms are europium. Oxygen are not drawn for the sake of clarity. (a) $\text{Hf}/(\text{Hf} + \text{Si}) = 20\%$, $\text{Eu} = 2.4 \text{ mol}\%$; and (b) $\text{Hf}/(\text{Hf} + \text{Si}) = 95\%$, $\text{Eu} = 4.9 \text{ mol}\%$.

Table 2

Coordination number for the first and the second coordination shell of europium

Hf/(Hf + Si) (%)	Eu–Eu at 4.5 Å	Eu–Si at 4.3 Å	Eu–Hf at 4.5 Å	Eu–O at 3 Å
10	1.56	1.11	2.84	4.44
50	1.00	0.18	6.62	5.75
90	0.54	0.04	8.20	6.18

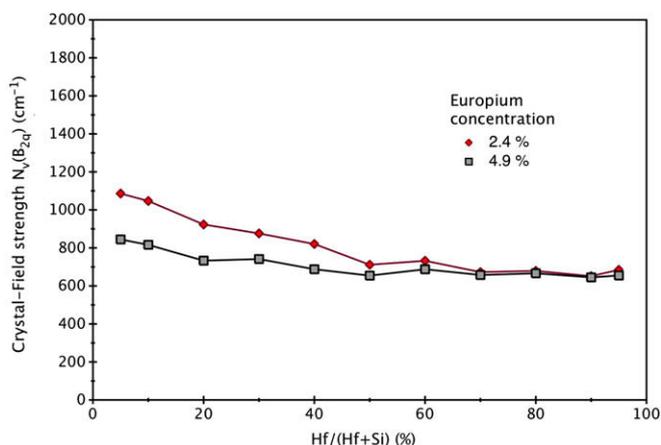


Fig. 7. Second order crystal-field strength $N_v(B_{2q})$ for simulated samples of the different concentrations. Each value is an average for all the rare earth ions in the calculated configuration.

Si in the second shell of Hf decreases from 4 to 2 with an increasing temperature of melting, whereas the number of Hf in the same shell increases from 4 to roughly 6. In a previous work, using ab initio modeling of smaller samples (117 particles) Ikeda et al. have found a phase separation between amorphous SiO_2 and HfO_2 [13]. Analysing radial distribution functions (RDF), not shown here, as well as snapshots (Fig. 6), it appears that Eu^{3+} ions prefer Hf-rich domain where they can find a larger amount of non-bridging oxygen to satisfy their high coordination number requirement. For instance, at a concentration of 50% of hafnium, and at a distance of 4.5 Å, Eu^{3+} is surrounded in average by 6.6 Hf and 0.2 Si (see Table 2). In a recent work, Afify et al. have performed X-ray absorption fine structure (EXAFS) measurements on Er^{3+} -doped silica waveguides codoped with different oxides, including hafnium oxide, and they conclude that for the studied concentration, ‘ Er^{3+} ions are mainly dispersed in an amorphous HfO_2 environment, thus explaining why the optical properties are strongly modified with respect to the pure silica wave-guides’ [14]. This conclusion is in agreement with the one that can be drawn from our simulations.

From the simulated samples it has been also possible to calculate the second order crystal field parameter using a point charge model. For details on the calculation see e.g., Chaussement et al. [15]. Calculated N_v values spread in the range 100–2000 cm^{-1} with a mean value of 800 cm^{-1} , showing significant difference according

to the different concentrations in hafnium. (Fig. 7). There is a noticeable difference between the two set of samples. For the lower europium concentration set, the crystal-field strength decreases markedly up to 50% of Hf. For the higher Eu concentration, it does not vary a lot. The decreasing values of N_v with an increasing Hf concentration is well explained by the dissolution of RE ions in hafnium oxide, giving to the RE ions a more symmetric and less distorted environment thanks to a larger amount of non-bridging oxygen. However such an effect is less obvious for the higher europium concentration set, but it can be explained by the fact that in this case, most of RE ions belong to clusters where the crystal-field is weaker than the one experienced by isolated ions in silica; increasing the Hf concentration leads to disperse RE ions, breaking RE clusters that should have for consequence to increase the crystal-field strength. But, as previously explained, the dilution of RE ions into hafnium oxide decreases the crystal-field strength. Consequently, for the higher concentrated set, the crystal-field strength does not vary a lot.

4. Conclusion

Using molecular dynamics simulations, we have found that SiO_2 – HfO_2 systems are subject to a phase separation. Such a result is in agreement with experiments. Moreover, the rare earth-doped simulated samples show that the rare earth ions prefer to adapt themselves inside hafnium rich domains. The analysis of both photoluminescence experiments and calculated crystal field parameters for numerical samples indicates that the influence of hafnium favors the existence of lower energy sites for the rare earth ions. These results could explain the favorable effect of hafnium in rare earth-doped silicate glasses.

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