

Local structure around Er in silica and sodium silicate glasses

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Extended X-ray absorption fine structure (EXAFS) and photoluminescence (PL) measurements have been performed on three different Er-doped glasses: silica and sodium silicate doped with Er in the molten phase, and silica doped by MeV ion implantation. All samples show a luminescent transition centered around a wavelength of $\lambda = 1.54 \mu\text{m}$, corresponding to an intra-4f transition of Er^{3+} . EXAFS data show that the Er ions have about six O first neighbors, at a distance of 2.26 Å in all systems. Both silica glasses show a second-neighbor Er–Si shell at 3.11 Å which is not seen in the sodium silicate glass. This difference is reflected in a difference in the PL spectra. The Er–O shell in the silica glass shows 0.01 Å² more disorder than that in the Na-loaded material. These findings are rationalized in terms of the network-modifying effect of Na. Both EXAFS and PL show no significant differences between silica samples prepared in the molten phase or by implantation. At an Er concentration of ~1 at.%, no direct Er–Er bonds are observed.

1. Introduction

Rare earths in insulating matrices have long been known to have potential for useful optical properties [1]. Some of the strong transitions (e.g. intra-4f) in rare earth ions involve very localized orbitals which interact minimally with the surroundings of the metal atom, providing the Er ion is incorporated at the right charge state. Thus, the absorption and emission bands of the rare earths can be very narrow and show long lifetimes even in a disordered, solid-state environment.

The case of Er in glass has attracted much interest lately because of the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition in Er^{3+} at a wavelength around 1.55 μm , coinciding with the low-loss window of standard optical telecommunications fiber. Recently, there has been a rapid development of devices incorporating Er-doped glass fibers and thin films for use in optical amplifiers and lasers [2–5].

In order for the Er atom to display the desired sharp energy levels, it must be in the +3 valence state. It is also desirable that there are no direct Er–Er bonds. Thus, it is interesting to know what the environment of the Er is in glassy matrices. In this study, we have performed photoluminescence

and extended X-ray absorption fine structure (EXAFS) measurements on Er in pure silica and Na silicate (NAS) glasses. EXAFS is one of the most direct measurements for measuring interatomic distances, and one of the few which can be applied for amorphous systems. We find that in pure silica glass the Er is six-fold coordinated to O, with Si as a second neighbor at a well-defined distance. This second-neighbor coordination is not observed in the NAS glass, which is interpreted in terms of the network-modifying effect of Na.

2. Experimental

2.1. Sample preparation

Two Er-doped silica samples were prepared as follows. A 2 mm thick silica soot film was deposited onto a 18 mm diameter silica rod using a $\text{SiF}_4\text{--O}_2$ gas mixture in a vapor-phase axial deposition torch employing an oxyhydrogen flame. After cooling, the samples were soaked in a solution of 10 g ErCl_3H_6 in either 20 cm³ H_2O and 130 cm³ propanol or 20 cm³ H_2O and 50 cm³

propanol. The two different volumes for the same ErCl_3H_6 weight resulted in two different Er concentrations in the samples. After soaking, the samples were sintered at 1600°C and then fire polished at 2200°C and cooled down in air. Rutherford backscattering spectrometry (RBS) was performed to measure the Er concentration in the near surface region. The Er surface concentration amounted to 0.3 at.% and 1.6 at.% for the two samples, respectively. These two samples yielded indistinguishable EXAFS patterns. Here, only the one with the lower Er content will be discussed. This sample is referred to below as 'bulk-doped'.

Another Er-doped silica sample was produced by ion implantation. Recently, we have shown that MeV ion implantation is a suitable technique for optical doping of micrometer thick silica films [6]. The substrate used in this study was a bulk silica sample, commercially known as Suprasil 1. It was implanted with 2.9 MeV Er ions at a total dose of 3.4×10^{16} ions/cm². The sample was implanted through a metal contact mask in order to reduce charging effects and was kept at room temperature. Under these implantation conditions the Er concentration profile, as measured by RBS, is Gaussian shaped with the peak at 1 μm depth, a full width at half-maximum (FWHM) of 0.5 μm and a peak concentration of 1.0 at.%. After implantation, this sample was thermally annealed in vacuum (10^{-6} Torr) at 900°C for 1 h.

The Na silicate (NAS) sample was produced by melting a mixture of Er_2O_3 , Na_2SiO_3 and SiO_2 in a 10:45:45 weight ratio, in a Pt crucible. This composition yields a nominal Er atom fraction of 1.15%. The melt was kept at 1400°C for 12 h. in order to homogenize. The sample was then cooled to room temperature in approximately 15 min. The Er surface concentration in this sample as measured by RBS amounted to 1.2 at.%.

2.2. Photoluminescence

Photoluminescence (PL) measurements were performed at room temperature, using the $\lambda = 488$ nm line of a 150 mW Ar^+ laser as a pump

source. Spectra were collected using a 0.75 m Spex monochromator and a liquid-nitrogen cooled Ge detector. The spectral resolution was 4 Å. The pump signal was mechanically chopped at 10 Hz and the signal was collected using a lock-in amplifier.

2.3. EXAFS

EXAFS measurements were carried out in fluorescence at the Er L_3 edge, using beamline X-15A at the National Synchrotron Light Source (Upton, NY, USA). In order to determine the interatomic distances from the EXAFS spectra, we used two model compounds for obtaining the electron scattering phaseshifts for Er-O and Er-Si: crystalline Er_2O_3 and an Er complex sold by Aldrich Chemical Co. [7] as a shift reagent under the name of Resolve-Al ErFOD: $((\text{C}_3\text{F}_7\text{C}(\text{O})\text{CH}_2(\text{O})\text{C}(\text{CH}_3)_3)_3\text{Er})$. The method of Marcus and Flood [8] was used to make a fluorescence-grade sample of the Er_2O_3 , while the ErFOD was dissolved in methanol and imbibed into filter paper. Both samples showed a uniform pink color, indicating a reasonably uniform Er density. The ErFOD sample was run at 8 K in order to eliminate attenuation of the EXAFS signal by Debye-Waller effect, while the other samples were run at room temperature.

EXAFS measurements of the Er_2O_3 showed the split Er-O shell (three O at 2.229 Å and three O at 2.317 Å) known from the crystal structure [9], so we could not use this material as an EXAFS model by itself. Instead, we used the ErFOD complex. This is known to consist of three bidentate ligands surrounding an Er atom [10] and the Er is thus surrounded by six oxygen atoms. We assumed that all six Er-O bonds share a common distance. Since we do not know the Er-O distance in ErFOD, we had to measure this distance before we could use ErFOD as a model for the electron phaseshifts. We did this by pretending that the oxide was an unknown, and fitting its split Er-O shell to that of ErFOD, with the constraint that the subshells are separated by 0.0875 Å as is known from the crystal structure, and assuming Er to be surrounded by six O atoms in the ErFOD. We find that a fit consistent with

the known distances is obtained by assuming the Er–O distance in ErFOD to be 2.294 ± 0.010 Å, with the error limits being those for which the sum-squared residual is double the minimum value. The Er–O coordination number required of ErFOD for consistency with the fit is 7.76, which is higher than the known value of 6. This discrepancy may be due to the differences in chemical environment between Er oxide and the organic Er complex. Such chemical differences are known to affect EXAFS amplitudes from first-row scatterers, so we assume that this effective coordination number is appropriate for this model when measuring Er in an oxide-like environment.

In order to analyze the Er–Si shell, we used as a model compound a sample consisting of 2000 Å of Er deposited onto a Si(100) substrate, then annealed in vacuum for 7 h at 1200 °C. After annealing, reaction between the two layers had occurred. RBS showed that the laterally averaged Er content was 20 at.% near the surface, falling to zero within 1 μm of depth. The only phases detected by X-ray diffraction were Si and ErSi₂ [11]. The ErSi₂ has a first-neighbor coordination of 12 Si at 3.00 Å [12] around each Er atom.

The EXAFS analysis was carried out in the usual way, with k^2 weighting of the spectra [13]. For the silica samples, the two visible shells were taken together in filtering by using an extra-wide (2.4 Å FWHM) filter window.

3. Results

3.1. Photoluminescence

Figure 1 shows PL spectra of the Er-doped pure silica and NAS samples. All spectra peak at a wavelength around 1.54 μm, corresponding to the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition in Er³⁺. The spectra for the bulk-doped and implantation-doped silica samples look similar. However, the shape of the spectrum for the NAS sample is quite different, with side peaks around 1.49 and 1.63 μm and a splitting of the main peak at 1.54 μm.

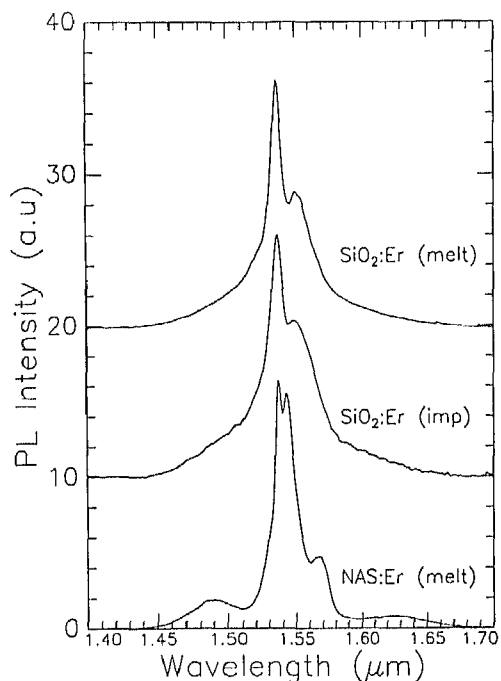


Fig. 1. Photoluminescence spectra of pure silica doped with Er in the melt (top), silica doped by ion implantation (middle) and sodium silicate glass doped in the melt (bottom). Spectra are taken at room temperature using a $\lambda = 488$ nm pump.

3.2. EXAFS

The Fourier transforms (FT) of the EXAFS spectra for all three samples are shown in fig. 2. The bulk-doped silica samples (fig. 2(a)) displayed two shells in the FT. The first shell works out to be 6.0 O atoms at 2.28 Å, with a mean-square fluctuation in bond lengths of 0.008 Å². The second shell is Er–Si, at a distance of 3.11 Å, and a coordination of at least 3. We cannot specify an upper limit for this coordination as one can increase the coordination number and increase the root mean-square (RMS) distance fluctuation without much change in the quality of the fit. If the coordination number is assumed to be 3, then the mean-square distance fluctuation is about 0.01 Å². If we fix the Er–Si coordination to be 6, we obtain a mean-square displacement of 0.023 Å².

The Fourier transform for the implantation-doped silica sample (fig. 2(b)) resembled that for

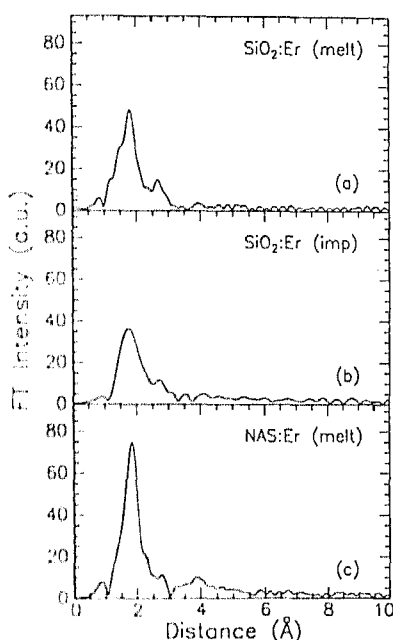


Fig. 2. Fourier transformed EXAFS data for pure silica doped with Er in the melt (a), silica doped by ion implantation (b) and sodium silicate glass doped in the melt (c).

the bulk-doped one, but with a slightly smaller Er–O distance (2.25 Å) and coordination number (5.5). A second shell is marginally visible in the FT at about the same place as in the FT for the bulk-doped silica, but the data were not sufficient for an analysis of this shell.

For the NAS sample (fig. 2(c)), the analysis is consistent with only a first shell, which can be analyzed as 6.3 O atoms at 2.26 Å, with no detectable disorder. The parameters for the first-neighbor Er–O shells for all three samples are summarized in table 1. The first neighbors differ mainly in the amounts of disorder ($\Delta\sigma^2$).

Table 1
Er–O distance ($R_{\text{Er-O}}$), coordination numbers (CN) and mean-square relative displacements ($\Delta\sigma^2$) for the three samples

Sample	$R_{\text{Er-O}}$ (Å)	CN	$\Delta\sigma^2$ (Å ²)
SiO ₂ :Er (melt)	2.28	6.0	0.008
SiO ₂ :Er (implant)	2.25	5.5	0.011
NAS:Er (melt)	2.26	6.3	0.0

No evidence was observed for direct Er–Er bonds in any of the three samples.

4. Discussion

Photoluminescence spectra are sensitive probes of the local environment of the Er ions. As is well established, local differences in the host electric field can give rise to differences in the Stark-split sublevels of the excited state and ground manifold [14]. Differences in local environment can also result in different inhomogeneous broadening of the spectra. The similarity in the PL data for the bulk-doped and implantation-doped silica samples suggests that the local environment around the Er ion is similar in those samples. This similarity is directly observed in the EXAFS data: the Er–O distance, standard deviation in the distance, and the coordination number are rather similar in the two glasses. The relatively large standard deviation in the Er–Si distances measured for the bulk-doped glass (0.023 \AA^2 for an Er–O coordination of 6) suggests that the Er is not directly bonded to Si, but is instead connected through a bridging atom, such as O. Taking this bridging model literally, we find an Er–O–Si bond angle of 104° , with an RMS fluctuation of about 7.8° . This estimate is obtained by considering the Er–O–Si triangle to have sides of length $3.10 \pm 0.15 \text{ \AA}$ (the second-neighbor bond with its RMS fluctuation), $2.28 \pm 0.09 \text{ \AA}$ (the first-neighbor bond), and 1.62 \AA (the measured Si–O distance in silica [15]). The fluctuations in bond angle caused by the fluctuations in the two bond lengths are added in quadrature. Most (7.5°) of the bond-angle fluctuation comes from the second-neighbor bond, with only 2.2° from the first-neighbor bond. This bond angle is near the tetrahedral value, and less than the usual Si–O–Si bond angle in silica glass (144° [16]). Figure 3(a) schematically depicts this configuration.

The shape of the PL spectrum for the NAS glass suggests that the local environment of Er in this material is different than that in the pure silica glass. Indeed, the EXAFS data show this difference: the Si second neighbor is not observed

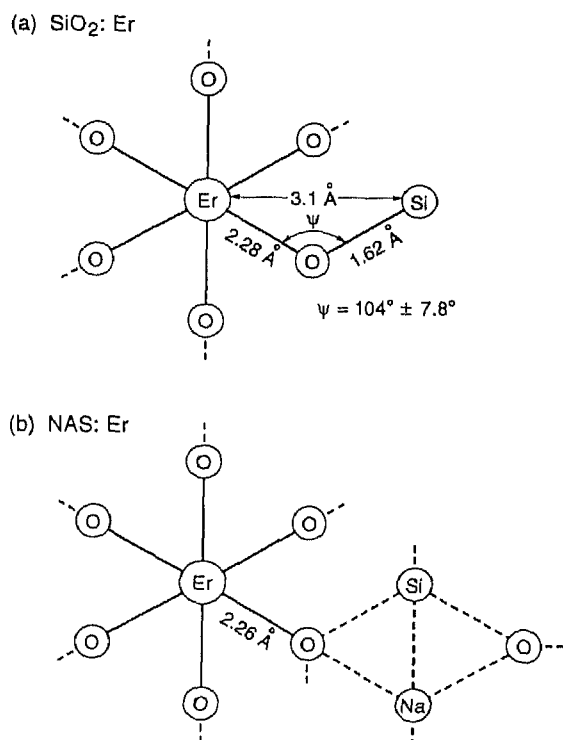


Fig. 3. Schematic representation of local environment around ER based on interpretation of the EXAFS data in pure silica (a) and NAS (b).

and the Er–O distance shows no detectable disorder. This can perhaps be understood with reference to the known effect of alkalis on silicate glass structure [17]. It may be that the Na⁺ ions break up the Si–O network and thus allow the ErO₆ moiety to relax to its lowest-energy state, free from forces applied by the Si–O network. In this model, the sodium acts as a ‘lubricant’, decoupling the Er–O group from the rest of the glass. This decoupling results in a narrower Er–O bond length distribution than that in pure silica. Since the Si, which is part of the network, is now decoupled from the Er, no Er–Si shell is observed. This is depicted schematically in fig. 3(b). The dotted lines in this figure are meant to indicate that there is probably some interaction between the Si, O, and Na ions, but their local geometry is variable and cannot be deduced from EXAFS data.

5. Conclusions

The local environment of Er ions in silica and sodium silicate has been determined. Photoluminescence spectra indicate a large difference between the local environment for Er in pure silica and sodium silicate glass, while no difference in environment is observed between silica doped in the molten phase or by ion implantation. These interpretations of the PL data are corroborated by EXAFS data. In all glasses, Er has six O first neighbors. The Er–O bond length distribution is greater in the pure glass than in the sodium silicate glass. Only in the pure glass is a second neighbor Si shell observed. The difference between the environment in the two glasses is interpreted in terms of the network-modifying effect of Na. For all samples the Er concentration is in the order of 1 at.%, and no evidence is observed for direct Er–Er bonds.

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