

The Site of Er in Phosphate Glasses Studied by K-Edge EXAFS

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Abstract. In the study of Rare Earth (RE) doped glasses for applications in optical amplifiers a key issue is represented by the role of local structure on the fluorescence lifetime τ . In particular clustering of the RE ions leads to a drop of τ and to a degradation of the device performances. K-edge EXAFS is particularly effective in revealing RE-RE coordinations as it permits to access the high k region ($k > 10 \text{ \AA}^{-1}$ where only the RE neighbors contribute to the spectrum). In this contribution we show an application of this experimental method to the study of Er-doped aluminophosphate glasses.

Keywords: Erbium doped glasses, High energy EXAFS

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INTRODUCTION

Rare earth (RE) doped glasses have attracted much attention due to their potential technological applications. In the case of Er^{3+} ions the optically excited luminescence originating from the dipole-forbidden $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition has a wavelength of $1.54\mu\text{m}$ that matches one of the minimum loss windows of commercial silica-based optic fibers. In the construction of integrated light amplifiers it is desirable to obtain the maximum gain within small component dimensions. It is experimentally proven that the gain g depends on the RE concentration c , increasing with c up to the so-called *quenching concentration* c_q after which it falls steeply. A proposed explanation for this phenomenon is that above c_q RE ions start to form small clusters. In this case due to the reduced RE-RE separation, the de-excitation of an optically excited ion can easily happen through a non-radiative energy transfer to a neighboring RE, thus lowering the lifetime of the fluorescence τ . Extensive studies on several insulating glasses doped with Er^{3+} ions show a typical c_q of 2 % [1]. Recent molecular dynamics calculations on Er^{3+} lead silicate glasses [2] suggest Er-Er clustering above 2 % Er. On the other hand, reverse Monte Carlo calculations, extended x-ray absorption fine structure (EXAFS), and wide angle x-ray scattering studies done on different glasses doped with Er [3, 4, 5, 6, 7], Tb [8, 9], Pr [10, 11], and other REs [12], have never detected any RE-RE correlation. This finding has been confirmed recently by carrying out XAS measurements at the RE K edges [10, 13, 14]. These experiments, making available the photoelectron wavevector range $k > 10\text{\AA}^{-1}$, better permit to evidence the RE-RE signal with respect to the L_{III} edges. Some

recent experiments, based on the method of isomorphic substitution in neutron diffraction [15], have, on the other hand, revealed RE-RE correlation in the cases of Dy and Ho $^{3+}$ ions. The reported RE-RE spacing is about 5.6 \AA , in substantial agreement with the 5.3 \AA deduced from the model of RE clustering proposed by our group [13]. In order to check if a RE-RE signal is directly visible in phosphate glasses we carried out an EXAFS experiment at the Er-K edge in 0.5-5 % bulk doped samples [4].

EXPERIMENTAL

Sample Preparation and Optical Measurements

RE (Er and Yb) doped alumino-phosphate glasses (indicative composition: $80P_2O_5$, $9Al_2O_3$, $5Li_2O$, $2B_2O_5$, $2BaO$, xRE_2O_3 , O/P ratio=2.8) were prepared from the melt, the RE concentration x ranging from 0.5% to 5% (See Tab.1). The x values were chosen to bracket c_q as shown in Tab.1 and in previously reported fluorescence lifetime data [4]. Samples have been optically characterized as a function of the RE concentration by measuring the $1.54\mu\text{m}$ emission lineshape (Fig. 1) and the fluorescence lifetime following laser excitation at 980 nm, where both Er and Yb ions show resonant absorptions [16]. The emission spectra of RE dopants in glass are reported to depend on the local environment as evidenced in [17]. The spectra of our samples shown in Fig. 1 all exhibit a similar shape, suggesting that the local site around Er does not change dramatically with the composition. On the other hand, the integrated absolute intensity has a maximum in the middle of the range and then decreases evidencing the quenching phenomenon.

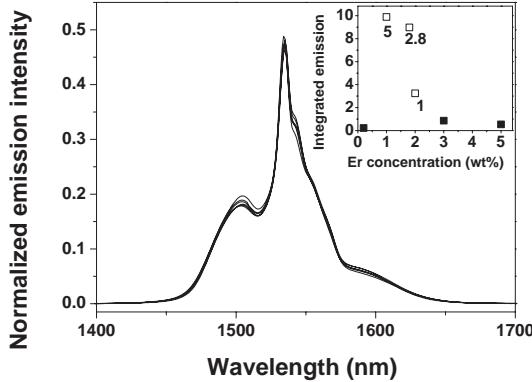


FIGURE 1. Normalized emission spectra collected at room temperature of the samples 1,2,4-6 obtained with an excitation at 980 nm. The inset shows the integrated absolute emission intensity.

EXAFS Measurements

EXAFS data at the Er-K edge ($E=57486$ eV) were collected at the GILDA beamline at the ESRF. Measurements at such high energies are not common as third generation synchrotron sources are needed to obtain sufficient flux from the machine. The monochromator was equipped with a pair of Si(311) crystals and were run in dynamically focusing mode [18]. A $250\mu\text{m}$ Cu filter was used to suppress the fundamental so only the third harmonic was present in the beam following the procedure described in [19]. This method permits to easily extend the energy spectrum of the monochromating system without carrying out any crystal change and avoiding working at low Bragg angles. A Kr filled ion chamber was used for signal normalization and a 13 elements High purity Ge detector was used to collect spectra in fluorescence mode. In order to reduce the fluorescence signal from the Ba-K series a 9 mm Al filter was placed in front of the detector: such filter exhibiting a transmission factor of 10 % for the Ba-K line and 40 % for the Er-K line permitted to optimize the ratio between the two signals. Measurements were carried out at 140 K in order to reduce thermal disorder. For each sample, 4 to 6 spectra were collected and averaged in order to improve the Signal-to-Noise ratio.

DATA ANALYSIS AND RESULTS

EXAFS data $\chi(k)$ were extracted using the ATHENA program [20]. The jump height was calculated from a fit of the edge to an arctan function as described in [19].

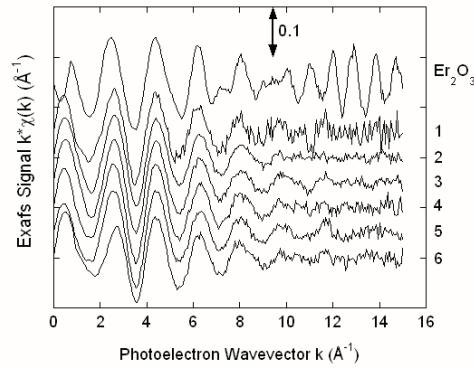


FIGURE 2. EXAFS spectra of the samples 1 to 6 compared with the spectrum of crystalline Er_2O_3 .

Theoretical signals were calculated with the FEFF 8.0 code [21] starting from a cluster of Er_2O_3 . Fits were carried out with the ARTHEMIS code [20] in k space in the interval $3\text{-}16\text{ Å}^{-1}$. The possibility of achieving such an extended k space range is the main advantage of using K edge in place of the usually used L_{III} edge. If we had used the Er- L_{III} edge ($E=8358$ eV) the available k range should have been less than 12 Å^{-1} due to the presence of the Yb- L_{III} edge at 8944 eV. The extracted XAS data are shown in Fig. 2. In this picture a comparison with the spectrum of crystalline Er_2O_3 is also provided. Note that a high frequency signal in the range $10\text{ Å}^{-1} < k < 18\text{ Å}^{-1}$ is evident that is due to Er-Er coordination. This region of the k space is particularly interesting because it permits easily to reveal a correlation between Rare Earth (RE) elements to be revealed without the complicating interferences of the signals from Er-O or Er-Si that are completely damped after $k > 9\text{ Å}^{-1}$. In the glass samples it is evident that no oscillations are evident above the noise in the region for $k > 10\text{ Å}$. The quantitative data analysis was carried out in k space by considering an Er-O path. The path was parametrized by the bond length R , number of O neighbors N and Debye-Waller factor σ^2 . Overall parameters like the edge shift E_0 and the extrinsic losses parameter S_0^2 were determined on the Er_2O_3 sample and kept fixed in the analysis of the samples. Same procedure was adopted for the σ^2 parameter. The results of the analysis are shown in Tab. 1. The quantitative data well reproduce the findings of our previous investigation at the Er- L_{III} edge [4] while permitting to exclude the presence of RE-RE coordination. A test, made by introducing such coordination in the fit, produced a coordination number of $N_{\text{Er}-\text{Er}} = 0 \pm 1$. On the other hand the considerable core hole width ($E=30$ eV, [22]) prevented us from detecting the long coordination Er-Si present at low k values that was instead well evidenced in the previous study [4].

TABLE 1. Results of the quantitative analysis of the EXAFS spectra. Data were fitted with a single Er-O shell. An attempt to include a further Er-Er shell gave a coordination number of 0 ± 1 . The values of the fluorescence lifetime are also reported in the last column.

Sample	Er (%)	Yb (%)	N	R ₁ (Å)	σ ₁ ² (Å ²)	Lifetime (ms)
1	0.2	-	6(1)	2.27(1)	0.0070	6.77
2	3.6	-	6(1)	2.25(1)	0.0080(4)	2.41
3	5	-	6(1)	2.25(1)	0.0070(4)	2.63
4	1	5	7(2)	2.26(1)	0.0080(4)	5.02
5	1.8	2.8	6(1)	2.25(1)	0.0070(4)	7.68
6	2	1	6(2)	2.26(1)	0.0070(4)	5.25
<i>Er₂O₃</i>	-	-	6	2.28(1)	0.0051(3)	-

DISCUSSION

From the XAS analysis it is clear that no significant changes in the Er site is observed at varying RE concentration x around c_q . All x Er is surrounded by roughly 6 O neighbors at a distance of ≈ 2.26 Å. No Er-RE coordination is visible passing from the lowest Er concentration (0.2 %) to the highest (5%) demonstrating that the RE clustering, evident from the values of fluorescence lifetime, does not take place at short distances. A similar result was obtained in alumino-silicate glasses analyzed both at the Er L_{III} [5] and Er-K [13] edges. Together with the results of the previous investigation [4] a common picture comes out with Er coordinated to PO_4 (or SiO_4) tetrahedra through a non-bridging oxygen. The Er-O distance is well defined as well as the Er-O-Si bond angle. A similar configuration has also been recently observed in Er + O doped Silicon [23]. The absence of Er-RE coordination suggests the absence of RE-RE or RE-O-RE configurations so the more compact way to "cluster" REs is via a whole PO_4 tetrahedron T, Er-T-RE. This model was already suggested in [13] and was shown to be capable to reconcile the absence of observable Er-RE coordination with the well defined site of Er. The present experimental data do not support the recent observation of a directly visible RE-RE correlation in orto-phosphate glasses made by neutron scattering [15].

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REFERENCES

1. F. Auzel, *Ann. Telecommun.* **24**, 199, ibid 363 (1969).
2. T. Peres, D. A. Litton, J. A. Capobianco, and S. H. Garofalini, *J. Non-Cryst. Solids* **221**, 34 (1997).
3. P. M. Peters, and S. N. Houde-Walter, *J. Non-Cryst. Solids* **70**, 541 (1997).
4. F. d'Acapito, S. Mobilio, P. Bruno, D. Barbier, and J. Philipsen, *J. Appl. Phys.* **90**, 265 (2001).
5. F. d'Acapito, S. Mobilio, P. Gastaldo, D. Barbier, L. Santos, O. Martins, and R. M. Almeida, *J. Non-Cryst. Solids* **293**, 118–124 (2001).
6. J. A. Sampaio, and S. Gama, *Phys. Rev. B* **69**, 104203 (2004).
7. M. Karabulut, G. K. Marasinghe, E. Metwalli, A. K. Wittenauer, R. K. Brow, C. H. Booth, and D. K. Shuh, *Phys. Rev. B* **65**, 104206 (2002).
8. D. T. Bowron, R. J. Newport, B. D. Rainford, G. A. Saunders, and H. B. Senin, *Phys. Rev. B* **51**, 5739 (1995).
9. F. Rocca, C. Armellini, M. Ferrari, G. Dalba, N. Diab, A. Kuzmin, and F. Monti, *J. Sol-Gel Sci. and Tech.* **26**, 267 (2003).
10. M. Braglia, G. Dai, S. Mosso, S. Pascarelli, F. Boscherini, and C. Lamberti, *J. Appl. Phys.* **83**, 5065 (1998).
11. F. Rocca, F. Monti, A. Kuzmin, A. Dalmaso, and D. Pasqualini, *J. Synchrotron Radiation* **6**, 737 (1999).
12. D. T. Bowron, G. A. Saunders, R. J. Newport, B. D. Rainford, and H. B. Senin, *Phys. Rev. B* **53**, 5268 (1996).
13. F. d'Acapito, S. Mobilio, L. Santos, and R. Almeida, *Appl. Phys. Lett.* **78**, 2676 (2001).
14. J. Cole, R. Newport, D.T.Bowron, R. Pettifer, G. Mountjoy, T. Brennan, and G. Saunders, *J. Phys. Condens. Matter* **13**, 6659 (2001).
15. R. Martin, P. Salmon, H. Fischer, and G. Cuello, *Phys. Rev. Lett.* **90**, 185501 (2003).
16. A. Speghini, R. Francini, A. Martinez, M. Tavernese, and M. Bettinelli, *Spectrochimica Acta A* **115**, 2001 (2001).
17. R. M. Almeida, and A. C. Marques, *J. Non-Cryst. Solids* **352**, 475 (2006).
18. S. Pascarelli, F. Boscherini, F. d'Acapito, J. Hrdy, C. Meneghini, and S. Mobilio, *J. Synchrotron Radiation* **3**, 147 (1996).
19. F. d'Acapito, S. Colonna, C. Maurizio, and S. Mobilio, *J. Synchrotron Radiation* **9**, 24 (2002).
20. B. Ravel, and M. Newville, *J. Synchrotron Rad.* **12**, 537 (2005).
21. A. Ankudinov, B. Ravel, J. Rehr, and S. Conradson, *Phys. Rev. B* **58**, 7565 (1998).
22. M. O. Krause, and J. Oliver, *J. Phys. Chem. Ref. Data* **8**, 329 (1979).
23. F. d'Acapito, S. Mobilio, S. Scalese, A. Terrasi, G. Franzò, and F. Priolo, *Phys. Rev. B* **69**, 153310 (2004).