| ESRF | **Experiment title:** EXAFS study of the local structure of luminescent erbium centers in titanosilicates | **Experiment number:** CH884 |
|---|---|---|
| **Beamline:** BM29 | **Date of experiment:** from: 2/2/00 to: 4/2/00 | **Date of report:** 12/7/00 |
| **Shifts:** 6 | **Local contact(s):** Michael Borowski | *Received at ESRF:* 28 JUIL. 2000 |

**Names and affiliations of applicants** (* indicates experimentalists):

**M. Pillinger*, J. P. Rainho*, J. Rocha, I. S. Gonçalves**

Departamento de Química, Universidade de Aveiro, Portugal

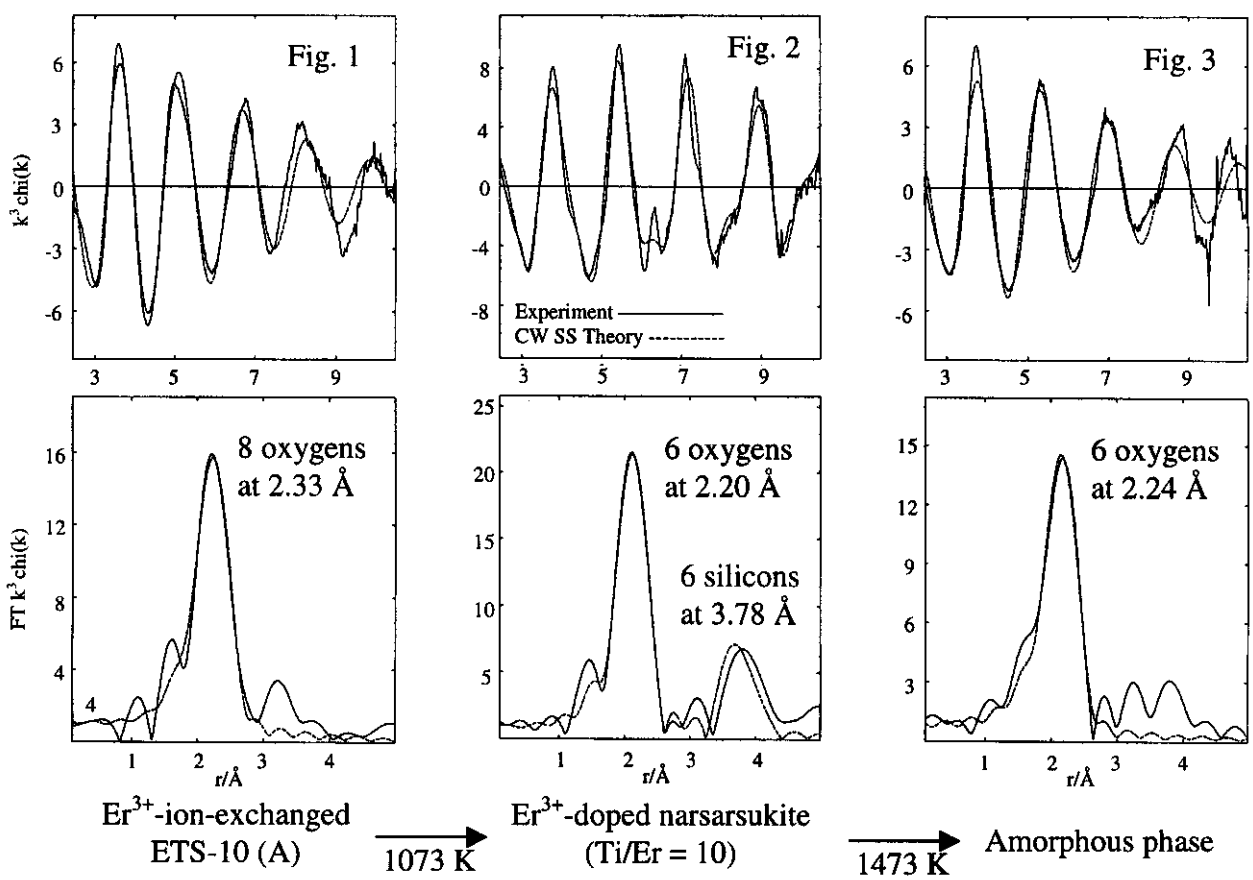
**Aims**. The microporous titanosilicate ETS-10 $[(Na,K)_2TiSi_5O_{13}\cdot xH_2O]$ doped with different concentrations of $Er^{3+}$ ions may be used as a precursor for preparing novel dense materials, analogues of the mineral narsarsukite $[(Na,K)_2TiSi_4O_{11}]$, which display a high and stable room-temperature emission in the visible and infrared spectral regions [J. Rocha *et al.*, *J. Mater. Chem.*, 2000, **10**, 1371]. Er $L_{III}$-edge EXAFS studies were carried out in order to probe the local erbium environment in these materials and gain a better understanding of their unusual optical properties.

**Experimental conditions.** Er $L_{III}$-edge X-ray absorption spectra were collected at room temperature (ca. $10^{-5}$ mbar) and/or 50 K (Oxford cryostat, He exchange gas) in transmission mode on BM29 at the ESRF, operating at 6 GeV in 2/3 filling mode with typical currents of 170–200 mA. [double crystal Si(311) monochromator, ion chamber detectors]. Spectra were recorded in the range 8.058–9.3 KeV (50% harmonic rejection, EXAFS scan with optimised energy mesh, 3 s per scan point). Powdered samples were diluted with appropriate amounts of boron nitride and 13mm diameter pellets prepared. A total of about 40 complete EXAFS scans were acquired for 11 different samples (r.t. and/or 50 K for each sample, 1-2 scans per sample). A reference sample of bulk $Er_2O_3$ was used as a model standard for determining coordination numbers and interatomic distances.

**Analysis.** Background subtraction and EXAFS curve-fitting analyses were carried out within the programs EXBACK and EXCURVE (version EXCURV98, Daresbury Laboratory, U.K.).

**Sample characteristics.** EXAFS spectra were measured for $Er^{3+}$-ion-exchanged ETS-10 samples calcined at 973 K, 1073 K, 1273 and 1473 K. $Er^{3+}$-doped narsarsukite crystallises at 973-1173 K, at ca. 1190 K the materials melt and at ca. 1473 K an amorphous phase is obtained. Two ETS-10 samples loaded with high (A) and low (B) amounts of Er were used that led to $Er^{3+}$-doped narsarsukite with Ti/Er = 10 and 23 respectively (ca. 4 and 2 mass% erbium).

**Results.** EXAFS spectra were of satisfactory quality up to 11 $Å^{-1}$ for samples A (edge jump ca. 0.15 a.u.) and up to 9 $Å^{-1}$ for samples B (edge jump ca. 0.05 a.u.). The spectrum of $Er^{3+}$-ion-exchanged ETS-10 (sample A, 50 K, Fig. 1) was adequately fitted by a single shell of 8 oxygens at 2.33 Å, presumably comprising at least some hydration water molecules ($2\sigma^2$ = 0.026 $Å^2$). $Er^{3+}$-doped narsarsukite, formed at 1073 K, provided a markedly different EXAFS spectrum and Fourier transform (Fig. 2). A well-defined shell of 6 oxygens could be fitted at 2.20 Å ($2\sigma^2$ = 0.008 $Å^2$) and an additional shell of 6 silicon atoms at 3.78 Å ($2\sigma^2$ = 0.012 $Å^2$). The Er···Si distance seems reasonable for Er–O–Si bonding. There was no evidence for Er···Er correlations within the short range order, a result especially pertinent to the optical properties of these materials. The average Er–O bond distance is significantly shorter than that for $Er_2O_3$ (6 O's at 2.26 Å, $2\sigma^2$ = 0.012 $Å^2$). These results suggest the existence of [$ErO_6$] complexes which are strongly bonded internally and weakly coupled to the narsarsukite lattice. The amorphous sample, formed at 1473 K, provided a different EXAFS spectrum and was found to have 6 nearest oxygen neighbours at 2.24 Å ($2\sigma^2$ = 0.017 $Å^2$) but no well-defined second nearest neighbour shell (Fig. 3). Comparable results were obtained with the samples containing a lower amount of erbium, indicating that the local environment around the $Er^{3+}$ centres was the same for differently loaded samples calcined to the same temperature.




**Acknowledgements.** We are grateful to the ESRF for the provision of facilities and to the BM29 team for their help and technical assistance during the running of our experiments.