



	Experiment title: Probing the niobium coordination in amorphous Nb ₂ O ₅ -SiO ₂ sol-gel materials with XAFS	Experiment number: CH-1609
Beamline: BM26A	Date of experiment: from: 24/9/2003 to: 26/09/2003	Date of report: 23/02/2005 <i>Received at ESRF:</i>
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Report:

Overview

Local structure about the niobium site was examined in a range of Nb₂O₅-SiO₂ xerogel samples using Nb K-edge EXAFS. Three separate (Nb₂O₅)_x(SiO₂)_{1-x} series of sol-gel samples with composition $x = 0.03, 0.075$ and 0.3 were prepared. These particular compositions were chosen since the first two are in the range of catalytic interest, and the $x = 0.3$ sample is well beyond the solubility limit of Nb₂O₅ in SiO₂, so that after sufficient heat treatment it will certainly contain some phase separated Nb₂O₅ and thereby acts as a calibration. The samples were studied as formed and then heated *ex situ* to 250, 500 and 750°C. As calibration, a set of crystalline niobates were also run including AlNbO₄, BaNb₂O₆, LaNbO₄, LiNbO₃, Nb₂O₅, the ferroelectric relaxor phase PMN and YNbO₄. The model compounds provided a range of niobium coordinations, i.e. NbO₄, NbO₅ and NbO₆, to compare with the niobium siting in the (Nb₂O₅)_x(SiO₂)_{1-x} sol-gel samples. The 'step-by-step' transmission EXAFS was collected at room temperature on BM26a at the niobium K-edge at 18986 eV. Data was successfully collected on all these samples.

Data Analysis and Results

The experimental data was processed using the suite of programs available at the Daresbury SRS. The raw data was normalised and repeat scans were summed using the program Excalib. The resulting files were then processed using Exback, which removes background contributions to the data. The fitting procedure was carried out using the program Excurv98, which uses curved wave and Rehr Albers theory to transform the parameters of the radial shells of atoms surrounding the central absorbing nucleus, to produce a theoretical absorption spectrum to match the experimental one. The parameters were varied until a fit is made for the data in the format ($\chi(k) \times k^3$) against k . This was then Fourier transformed to yield information in r -space.

There have been difficulties with fully analysing the data. There seems to be a physically unfeasible peak at ~ 1.3 Å. Unfortunately this peak cannot be resolved from the Nb-O peaks at roughly 1.7 Å and 1.95 Å, and it appears as a hump on the low- r side of the expected peaks. The inability to resolve this unexpected peak from our physically useful peaks has made it difficult to obtain accurate values for bond distance and co-ordination number. It is interesting that in a separate experiment on station 9.2 at the SRS the same feature was observed. Several avenues have been explored whilst trying to discover the cause of this extra peak,

including double excitation and multiple scattering effects. However, it is now thought that perhaps the problem is simply that the background, subtraction performed by the program Exback was insufficient to completely remove background absorption effects. It is now planned to attempt to remove the background using the spline-tool within Matlab. This should allow a greater degree of flexibility and user input when removing the background and will hopefully result in our ability to fully analyse this EXAFS data. Some preliminary r-space data is shown in Fig. 1 for 3% and 30% niobium-containing samples heated to 750°C.

Figure 1. Nb K-edge EXAFS of sol-gels heated to 750°C (a) $(\text{Nb}_2\text{O}_5)_{0.03}(\text{SiO}_2)_{0.97}$ and (b) $(\text{Nb}_2\text{O}_5)_{0.30}(\text{SiO}_2)_{0.70}$

The data shows a well defined Nb-O peak (with the shoulder at very short distances). The peak is a composite of different Nb-O bond lengths. The spectra show that there is definite evidence of longer bond lengths for the 30% Nb₂O₅-containing sample which also has a stronger second coordination peak. This all fits with phase separation of Nb₂O₅ in this sample. This is a similar type of behaviour to when titania is added to silica.

1. K.O. Drake, D. Carta L. Skipper, F.E. Sowrey, R.J. Newport and M.E. Smith, Solid State NMR, 27 (2005) 28-36.