An extended x-ray absorption fine structure study of the rare earth sites in a neodymium doped glass

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The local environment around the metal sites in a Nd doped aluminosilicate glass has been determined using extended x-ray absorption fine structure. Detailed fitting of the spectrum reveals an average Nd coordination of 4·5 ± 1 oxygen atoms at 2·15 Å and 4·5 ± 2 oxygen atoms at 2·44 Å; a second shell, containing silicon atoms, is centred at 3·7 Å. It is suggested that all the oxygen atoms are nonbridging.

Interest in rare earth doped glasses has increased over recent years—a trend fuelled, at least in part, by their central role in the development of fibre lasers, optical amplifiers, optical switches, nonlinear devices, and

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intrinsic fibre sensors.[1] Considerable contemporary interest has focused on the attributes of the Nd doped silicates, which are of central concern here.

The optical properties induced by the rare earth ions are dependent on the type of host glass in which they are incorporated. For instance, the addition of a network modifier such as aluminium or phosphorus into a silicate glass would appear to allow Nd contents as high as 7 wt% before clustering or phase separation effects are observed using fluorescence decay rate studies.[2,3] A detailed understanding of the nature of the rare earth sites is therefore of great importance in the study of these systems. We report here the preliminary results of a novel programme of structural studies centred on x-ray scattering techniques; in particular we report the first chemically specific extended x-ray absorption fine structure data on a Nd doped aluminosilicate optical fibre preform.

Experimental

The single glass sample investigated in this study was fabricated by a solution doping technique;[4] neodymium ions being incorporated into the aluminosilicate host glass to give approximately 4 wt% Nd. (Refractive index profiles indicate an Al_2O_3 codoping level of ~6 wt%.)

The measurements, at the Nd L_3 edge (6208 eV) were performed on beamline 8·1 at the SRS, Daresbury Laboratory. Monochromation of the incident x-ray beam was achieved using an order sorting double crystal Si{111} monochromator with focusing optics. Structural information was obtained by multiparameter fitting of the experimental data to the extended x-ray absorption fine structure function in k space using the least squares routine available in the EXCURV90 package;[5] this is based on a fast curved wave theory.[6] The principal elements of this data analysis process are given by Edwards *et al.*[7]

Results and discussion

In Figure 1 we plot the k^3 weighted extended x-ray absorption fine structure function against photoelectron wavenumber, k; Figure 2 shows the corresponding Fourier transform. In both Figures the theoretical fit is plotted with the experimental curve. The Fourier transform is phase corrected to give peak positions corresponding to true interatomic distances. Figure 2 provides clear evidence for a split first shell, which we ascribe to oxygen neighbours, and a second shell, which is probably due to silicon. Detailed fitting of the spectra gives an average Nd coordination of $4·5 \pm 1$ atoms at $2·15 \pm 0·02$ Å with a mean square deviation $\sigma_1^2 = 0·05$ Å^2, and $4·5 \pm 2$ oxygen atoms at $2·44 \pm 0·02$ Å with a mean square deviation $\sigma_2 = 0·03$ Å^2. The second shell could not be fitted in detail with reasonable statistical significance but is consistent with the presence of approximately three Si atoms at a distance ~3·7 Å. We note that the Nd environment in the glass differs somewhat from that found in the $Nd_2O_3 \cdot Na_2O_2 \cdot SiO_2$ crystal,[8] which comprises two oxygen atoms at ~2·3 Å plus another five or six between 2·4 and 2·5 Å. The silicon neighbours

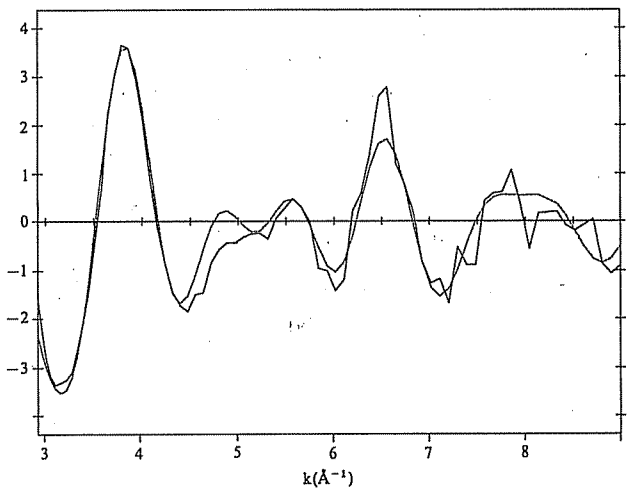

Figure 1. *The Nd L_3 edge extended x-ray absorption fine structure spectrum, weighted by* k^3
——— experiment – – – – – theory

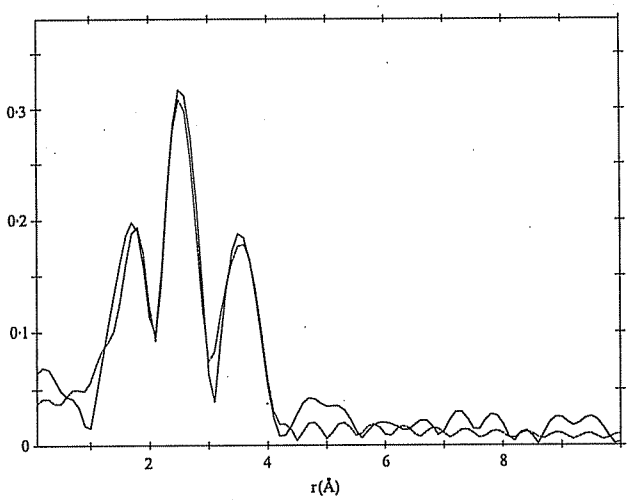

Figure 2. *The Fourier transformed extended x-ray absorption fine structure function*
——— experiment – – – – – theory

in the crystal lie between 3 and 4 Å from the Nd; the extended x-ray absorption fine structure data on the glass is barely able to resolve those Si atoms bonded to the highly disordered near oxygens, and we suggest that there will be further silicon atoms at ~4 Å associated with the long bonded oxygens. The spectrum in Figure 2 does show some intensity in this region, but it is not statistically significant.

The mean square deviations associated with the oxygen distances in the glass are far too large to be due to thermal vibrations. Rather, they represent a statistical distribution of distances within the shell. Thus, with $\sigma_2 = 0·17$ Å we may conclude that the long bonded oxygen atoms actually lie between 2·3 and 2·6 Å from the neodymium, a somewhat wider range than is found in the crystal. The great majority of the oxygen neighbours of neodymium in the crystal are nonbridging, and each oxygen is linked to a different silicon atom. From a consideration of the simple modified random network model of glass structure,[9] is is also reasonable to conclude that all the oxygen neighbours of Nd in the glass will be nonbridging.

Concluding remarks

We have demonstrated the usefulness of the chemical specific structural probe provided by extended x-ray absorption fine structure in a preliminary study of a Nd doped aluminosilicate glass. The technique has yielded detailed information on the near neighbour environment of the rare earth. An experimental programme is now under way which will not only provide data as a function of rare earth content but will, using a pinhole collimator geometry, also enable spatially resolved data to be gathered across the diameter of the core of the optic fibre preform.

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