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NXFit: a program for simultaneously fitting X-ray and neutron diffraction pair-distribution functions to provide optimized structural parameters

David Pickup, Robert Moss and Robert Newport


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**NXFit:** a program for simultaneously fitting X-ray and neutron diffraction pair-distribution functions to provide optimized structural parameters

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**1. Introduction**

Since the atomic structure of materials often plays a key role in determining their physical properties, knowledge of how the atoms are arranged is fundamental to materials science. Diffraction has become an important tool for determining the atomic scale structure of materials, and advanced instrumentation has made the collection of high-quality data possible. However, analysis and interpretation of that data can still be difficult, particularly where the material has a complicated structure and/or multiple components. There are various approaches to fitting data from crystalline materials, the most common of which is Rietveld (1969) refinement, which can be applied to both X-ray and neutron diffraction data. Fitting diffraction data from amorphous materials is more problematic, and different processes have been formulated. One method is to prepare atomistic models and to refine these against the experimentally obtained diffraction pattern. This is the approach adopted in reverse Monte Carlo (RMC) modelling (McGreevy & Pusztai, 1988; McGreevy, 2001) and, more recently, in empirical potential structure refinement (Soper, 2001, 2005). Another method is to calculate the model, for example using molecular dynamics simulations (Alder & Wainwright, 1959; Cormack & Cao, 1996), and then compare aspects of this model with those from the experimental data.

An alternative approach is to convert the diffraction data into a real-space pair-distribution function by Fourier transformation and fit this function with a series of peaks that simulate the correlations between pairs of atoms. This method has been applied successfully to both crystalline (Hannon et al., 2008) and disordered materials (Hoppe et al., 1995). An advantage of this method is that it is possible to simultaneously fit X-ray and neutron data from the same sample using a single set of structural parameters. This feature is particularly useful when fitting data where there are a large number of overlapping correlations (in a multicomponent glass for example), because the relative contribution of each atomic pair to the data is different for X-rays and neutrons. X-rays interact with the electrons in the atoms and preferentially pick out high-Z elements, whereas neutrons interact with the nuclei in the sample and the scattering strength does not exhibit a monotonic trend with atomic number.

Whilst programs such as PDF2 and PDFgui (Farrow et al., 2007) are available to fit theoretical three-dimensional structures to atomic pair-distribution functions from crystalline materials, the modelling of such data from amorphous materials is more difficult. The program presented here, NXFit, automates the fitting of pair-distribution functions from amorphous materials and is capable of fitting X-ray and neutron scattering data simultaneously. The user specifies a set of initial structural parameters, atom types and distances, coordination numbers, and disorder parameters to describe the correlations between the pairs of atoms present in the structure. These are used to generate partial correlation functions in $Q$ space, which are summed before Fourier transformation for comparison with the experimental pair-distribution function. The parameters are then refined until a satisfactory fit to the experimental data is achieved. The advantage of generating the simulation in $Q$ space is that, provided the same Fourier transform range is used for the data and the simulation, truncation effects due to the finite range of the data in $Q$ space can be ignored.

The application of NXFit is demonstrated by fitting both X-ray and neutron diffraction data from two very different amorphous materials: a sodium metaphosphate glass prepared by melt quenching a molten mixture of oxides and a mixed TiO$_2$–SiO$_2$ glass prepared by a low-temperature sol–gel route.

**2. Theory and data analysis**

In order to obtain structural information from neutron diffraction data, it is first necessary to perform corrections for background scattering, absorption and multiple scattering to determine the differential cross section (Hannon et al., 1990):

$$\frac{d\sigma}{d\Omega} = I(q) + I_s(q),$$

(1)
where \( Q = 4\pi \sin \theta / \lambda \), (2\( \theta \) is the scattering angle and \( \lambda \) is the neutron wavelength), \( f_i(Q) \) is the self-scattering and \( i_i(Q) \) is the structure-dependent part of the data. The self-scattering term can be calculated (Wright, 1985) and subtracted to yield the interference function \( i_i(Q) \).

Similarly, with X-ray diffraction the measured scattering intensity is corrected for polarization and absorption effects, background scattering, and Compton scattering to yield \( \mathrm{d}Q/\mathrm{d}\Omega \). The structure-dependent interference function \( i_i(Q) \) can then be extracted from \( \mathrm{d}Q/\mathrm{d}\Omega \) (Pings & Waser, 1968):

\[
i_i(Q) = \frac{\mathrm{d}Q}{\mathrm{d}\Omega} - \sum_i c_i f_i(Q)^2.
\]

where \( f_i \) are the \( Q \)-dependent atomic scattering factors, \( c_i \) are the atomic fractions of the components and \( n \) is the number of atom types.

When fitting neutron and X-ray data simultaneously, it is beneficial to normalize each \( i_i(Q) \) to have the same units before transformation to the real-space pair-distribution function. This can help prevent scaling problems and is required when using NXFit. If \( a_i(Q) \) is introduced to represent either the neutron scattering length \( b \) or the X-ray scattering factor \( f(Q) \), the total scattering structure factor is defined as (Keen, 2001)

\[
S(Q) - 1 = i_i(Q) \left[ \sum_i a_i(Q)^2 \right].
\]

When dealing with X-ray data, the denominator of equation (3) is sometimes referred to as the sharpening function. Some workers use \( \sum_i c_i f_i(Q)^2 \) as the sharpening function, and others use \( c_i f_i(Q)^2 \). Care must be taken to use the former when preparing data to be used with NXFit.

Useful structural information can be extracted by Fourier transformation of the structure factor to the total correlation function \( T(r) \):

\[
T(r) = 4\pi \rho_0 r + (2/\pi) \int_0^\infty Q[S(Q) - 1]M(Q) \sin(rQ) \mathrm{d}Q.
\]

where \( \rho_0 \) is the macroscopic number density, \( r \) the scalar distance between pairs of atoms and \( M(Q) \) a modification function that takes into account that data cannot be collected over an infinite \( Q \) range. The simplest modification function is a step function, which is unity for \( Q \leq Q_{\text{max}} \) and zero for \( Q > Q_{\text{max}} \). This is equivalent to using no modification function at all and results in termination ripples on either side of the peaks in \( T(r) \). Such termination ripples can be suppressed by using a modification function that slopes more gently to zero. The two that can be used in conjunction with NXFit are the Lorch (1969) function,

\[
M_{\text{lorch}}(Q) = \begin{cases} 
\sin(Qr)/Qr, & Q \leq Q_{\text{max}}, \\
0, & Q > Q_{\text{max}},
\end{cases}
\]

and the Hanning window function (Yarker et al., 1986),

\[
M_{\text{hanning}}(Q) = \begin{cases} 
1 + \cos(\Delta rQ)/2, & Q \leq Q_{\text{max}}, \\
0, & Q > Q_{\text{max}}.
\end{cases}
\]

where \( \Delta r = \pi/Q_{\text{max}} \). Both have the effect of reducing termination ripples but at the expense of real-space resolution.

\( T(r) \) can be described as a weighted sum of the partial correlation functions \( t_{ij}(r) \):

\[
T(r) = \sum_{i,j} c_{ij} a_i(Q) a_j(Q) t_{ij}(r).
\]

where the \( i, j \) summations are each over the elements in the sample. The weighted partial correlation functions manifest themselves as peaks in \( T(r) \), with positions corresponding to interatomic distances between pairs of atoms and areas that represent the coordination numbers of these atomic pairs. In disordered materials all but the peaks representing the nearest-neighbour distances overlap with other peaks, and it becomes necessary to deconvolve the contributions from each atomic pair to yield structural information. This can be achieved using an approach based on the Debye scattering equation, which gives the average scattering from an array of atoms that takes all orientations in space (Warren, 1990):

\[
i_i(Q) = \sum_{m,n} a_m(Q) a_n(Q) \sin(Qr_{mn})/(Qr_{mn}).
\]

where \( m \) and \( n \) are the atoms in the array and \( r_{mn} \) the distances of each atom from every other atom.

By ascribing a Gaussian-type distribution to the interatomic distances, we can derive the pair function \( p_{ij}(Q) \), which can be used to model each \( t_{ij}(r) \) in \( Q \) space:

\[
p_{ij}(Q) = \frac{N_{ij} w_{ij}(Q) \sin(Qr_j)/Qr_j}{\left( \frac{Q^2 - \sigma^2_j}{2} \right)}.
\]

where \( N_{ij}, R_{ij} \) and \( \sigma_{ij} \) are the coordination number, atomic separation and disorder parameter (i.e. a measure of the thermal and static disorder), respectively, of atom type \( i \) relative to atom type \( j \). The weighting factors \( w_{ij} \) are the probe-dependent quantities given by

\[
w_{ij} = \frac{(2 - \delta_{ij}) c_i a_i(Q) a_j(Q)}{\left( \sum_{i,j} c_i a_i(Q)^2 \right)}.
\]

where \( \delta_{ij} \) is the Kronecker delta function (i.e. \( \delta_{ij} = 1 \) for \( i = j \) or \( \delta_{ij} = 0 \) for \( i \neq j \)) and \( a_i \) is the probe-dependent term: either the \( Q \)-independent neutron scattering length \( b \) or the \( Q \)-dependent X-ray scattering factor \( f(Q) \).

Individual \( p_{ij}(Q) \) functions can be calculated for each pair of atoms, summed and Fourier transformed for comparison with \( T(r) \) (Bruni et al., 1995). The advantage of simulating \( T(r) \) in this way is that the Fourier transformation is the same for both the data and the fit, negating the effects of the finite upper limit of \( Q \), providing the same \( Q \) range and modification function is used in each case. The values of \( N_{ij}, R_{ij} \) and \( \sigma_{ij} \) are varied to optimize the fit to the experimental data: the use of NXFit provides a convenient method to achieve this optimization.

3. Program details

NXFit was written in MATLAB (The MathWorks, Natick, MA, USA) but has been compiled to run alongside the MATLAB Compiler Runtime (MCR) on an end-user’s machine. Both Linux and Windows versions are available free of charge to academic users at http://www.kent.ac.uk/physical-sciences/software/nxfit/nxfit.html. NXFit uses the Nelder–Mead (also known as the ‘downhill’ or ‘amoeba’) method, which is a commonly used nonlinear optimization algorithm, to vary a set of ‘best guess’ parameters to achieve a fit to experimentally derived data. The scheme was developed by Nelder & Mead (1965) and is a numerical method for minimizing an objective function in an \( N \)-dimensional space. The method uses the concept of a simplex, which is a polytope with \( N + 1 \) vertices. For example, in one dimension the polytope is a line segment, in two dimensions it is a triangle and in three dimensions it is a tetrahedron. As the dimensionality of the problem increases, the polytope becomes more complex. The Nelder–Mead simplex method finds, approximately, the solution to a problem with \( N \) variables when the objective function

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Figure 1
Initialized NXFit GUI with all fields completed and ready to start the simulation. Plots in the right-hand panels show the experimental data (blue lines) and simulated fits (red lines).

varies smoothly. In the case of NXFit, the objective function is the combination of peaks that are being used to simulate the experimental \( T(r) \) and the value of interest to the optimization routine is the least-squares fit index, \( \text{FI} \):

\[
\text{FI} = \frac{\sum_{r \in \text{range}} \left( w^E \left( T^E(r) - T^S(r) \right) \right)^2 + w^N \left( T^N(r) - T^S(r) \right)^2}{\text{range over which the data is simulated}},
\]

where the subscripts \( E \) and \( S \) denote, respectively, the experimental and simulated correlation functions, the superscripts \( X \) and \( N \) refer to either \( X \)-ray or neutron, \( R_{\min} \) and \( R_{\max} \) define the range over which the data is simulated, and \( w^X \) and \( w^N \) are weighting factors that can be used to preferentially weight one data set over the other during the fitting process (see below). The value of \( \text{FI} \) is determined at each vertex of the polytope. In the simplest case, the point that yields the worst \( \text{FI} \) value is rejected and a new test point is developed by reflecting the simplex through the centroid of the remaining \( N \) points. If the new point is much better, then the simplex stretches out exponentially along this line. However, if the new point is not much better than the original test point, then the algorithm assumes that it is stepping across a valley and shrinks the simplex towards the best point. An occasional problem of multidimensional optimization algorithms is that they can become stuck in local minima because of the collapse of the simplex. The Nelder–Mead method is not immune in this regard (McKinnon, 1998). The standard approach to handling this is to arrange a new simplex starting from the current best parameter values. There are alternatives to Nelder–Mead, such as the flexible polyhedron method, but this tends to make a large number of unnecessary steps in regions of little interest and takes longer to converge on a solution.

In NXFit the Nelder–Mead method is implemented through the MATLAB function \texttt{fminsearch}, which uses the simplex algorithm as described by Lagarias et al. (1998). The behaviour of the simplex during the optimization is controlled by the parameters \( \alpha \), \( \gamma \), \( \rho \) and \( \sigma \), which are the reflection, expansion, contraction and shrink coefficients, respectively. The function \texttt{fminsearch} uses values of \( \alpha = 1 \), \( \gamma = 2 \), \( \rho = 0.5 \) and \( \sigma = 0.5 \).

The Nelder–Mead routine alone does not have any capacity to include constraints, but in order to fit experimental diffraction data it is necessary to constrain the fitting parameters to avoid nonphysical solutions. Upper and lower bounds are implemented with a wrapper function called \texttt{fminsearchbnd}, \(^1\) which sits on top of \texttt{fminsearch} and uses a sinusoidal transformation of the parameters:

\[
y(i) = \text{LB}(i) + \frac{1}{2} \left[ \text{UB}(i) - \text{LB}(i) \right] \sin[z(i)] + 1,
\]

where \( y(i) \) is the real parameter, \( z(i) \) is the transformed parameter, and \( \text{UB}(i) \) and \( \text{LB}(i) \) are the upper and lower bounds of \( y(i) \), respectively. It is clear from equation (12) that if \( z(i) \) is unconstrained and can have any value \( -\infty \leq z(i) \leq +\infty \), \( y(i) \) is restricted to the range \( \text{LB}(i) \leq y(i) \leq \text{UB}(i) \).

4. Using NXFit

NXFit has a graphical user interface (GUI) to enable the user to set the operating parameters easily. Fig. 1 shows a completed example of this GUI in an initialized state ready for a simulation to begin. As can be seen from Fig. 1, the user has to specify the name and path of the various data files and parameter files used in the fitting process and supply other relevant parameters.

\(^1\) \texttt{fminsearchbnd} was created by John D’Errico of the MATLAB user community and can be freely downloaded from the MATLAB file exchange: http://www.mathworks.co.uk/matlabcentral/fileexchange/8277-fminsearchbnd-fminsearchcon.
A parameter file containing the initial values of $R_{ij}$, $N_{ij}$ and $\sigma_{ij}$ for each correlation must be supplied, together with a file containing the constraints for each parameter, i.e. how much they can vary during the optimization.

The experimental data should be Fourier transformed according to equation (4). Since NXFit generates the pair function $p_i(Q)$ [equation (9)] before Fourier transformation into $r$ space to allow comparison with the experimental $T(r)$, the range over which the experimental data was Fourier transformed and the type of window function used must be specified. If both neutron and X-ray data are to be fitted simultaneously, the relative weighting of the two data sets can be entered.

In order to calculate $T(r)$, NXFit needs to know the composition of the sample and the scattering strengths of the atoms present. This information is supplied by the user in the form of a scattering factor file. In the case of neutron data, the scattering factor file contains the atomic number, average neutron scattering length and atomic fraction for each element in the sample. When fitting X-ray data, the neutron scattering length is replaced with the coefficients $a_i, b_i$ and $c_i$, which are used to generate the X-ray scattering factors via the following equation:

$$f_i(Q) = \sum_{i}^4 a_i \exp(-b_i s^2) + c,$$

(13)

where $s = Q/4\pi$. Values for $a_i, b_i$ and $c$ are tabulated in *International Tables of Crystallography* (Brown et al., 2006) and by Cromer & Mann (1968).

NXFit allows the user to specify the range in $r$ space over which the experimental $T(r)$ is to be simulated and the spacing in $Q$ used when $p_i(Q)$ is generated. When using NXFit, it is not usual to fit $T(r)$ beyond 4 Å because the problem of overlapping correlations makes it very difficult to assign features to particular pairs of atoms. The maximum number of iterations to be used in the fitting process can also be specified.

NXFit produces two or three output files depending on how many data sets have been used. These are a $T(r)$ file for each data set and a file containing the optimized parameters. The fit contains the original experimental $T(r)$ and the simulated $T(r)$, together with the partial correlation functions that it comprises (i.e. the contributions from the individual pairs of atoms).

Like any program, NXFit is not without its limitations. Particular care must be taken when preparing the initial parameter file since this is the point at which the user ascribes the various features in $T(r)$ to particular atomic correlations. Mistakes here can lead to nonsensical results later. To help with these assignments, it is often useful to look at the atomic distances present in crystals of similar composition and to examine in the results of studies of similar amorphous samples. It is also beneficial to bring in data from other techniques, for example EXAFS or NMR. Although the setting up of the initial parameters file can be problematic, it does allow for the refinement of parameters for mixed coordination sites, albeit in an indirect manner. If the coordination numbers of the environments, separate correlations can be set up for each environment and the parameters refined. If the coordination numbers of the sites are known, the relative abundance of each site can be calculated from the observed coordination numbers obtained from the refinement. For example, if a material contained a metal residing in two environments with respect to oxygen, fourfold or sixfold coordination, and the refined coordination numbers for these two correlations came out as 2 and 3, respectively, the calculated occupancy of both sites would be 0.5. The use of this approach has been demonstrated for aluminium-containing phosphate-based glass where aluminium resides in four-, five- and sixfold environments (Smith, King et al., 2013). Good agreement was obtained between neutron diffraction results and those from $^{27}$Al NMR.

At present NXFit does not calculate the errors associated with the optimized output parameters. However, the robustness of the fit can be tested by fitting the data with different starting parameters and taking the difference between the output parameters obtained from the two fits as estimates of the errors (Barney et al., 2011). This approach has been adopted here in the two examples of the application of NXFit.

### 5. Application to diffraction data from a sodium metaphosphate glass

Phosphate-based glasses have a variety of composition-dependent properties, which have led to their development for a range of specialty applications including nuclear waste containment (Day et al., 1998), fast ion conductors in solid state electrolytes (Bates et al., 1992), hermetic seals (Brow et al., 1995) and high-power lasers (Weber, 1990). Understanding the structure of such materials is therefore very important in optimizing their atomic properties. Here we describe the use of NXFit to fit both neutron and X-ray diffraction data from a melt-quenched (Na$_2$O)$_{0.5}$(P$_2$O$_5$)$_{0.5}$ metaphosphate glass.

This material is important because it is both biocompatible and bioreabsorbable (Knowles, 2003; Abou Neel et al., 2009).

The neutron diffraction data were collected on the GEM diffractometer at the ISIS spallation neutron source at the Ruther-
Na—O distance to be 3.0 Å. A study of (CaO)_{0.5}(P_2O_5)_{0.5} glass by
neighbour distance to be 2.9 Å and the second nearest-neighbour
the basis of recent RMC modelling studies of metaphosphate glasses.
These changes were made on
inclusion of the X-ray data and to changes to the assignment of some
previous neutron study of (Na_2O)_{0.5}(P_2O_5)_{0.5} (Pickup
refined parameters used to generated these fits are given in Table 1.
replaced by an Na—Na distance of 2.89 Å and a second nearest-
neighbours across the BOs. These key features are
reflected in the parameters in Table 1: the P—BO and P—P coordi-
nation numbers are 2 within experimental error and the P—NBO
coordination number is close to two. Furthermore, fitting with NXFit
also identifies some of the more subtle features of the metaphosphate
glass structure. The neutron data were collected over a wide Q range
(Q_max \approx 60 Å⁻¹), which results in excellent real-space resolution and
allows the distinct P—NBO and P—BO distances to be resolved. This
is illustrated by Fig. 3, which shows the contributions of the P—NBO
and P—BO partial correlation functions to the neutron T(r) in the
range 1–2 Å as output by NXFit. The P—NBO bond distance is
shorter than the P—BO bond length because the former has a degree of
double-bond character (Hoppe et al., 2000). The other interesting
feature of the structure of (Na_2O)_{0.5}(P_2O_5)_{0.5} becomes clear if the
number of NBOs per Na⁺ is considered alongside the Na—O coordi-
nation number. The former is 2 and the latter, as determined here and
in excellent agreement with the previous study by Hoppe et al.
(1995), is 5. Assuming the sodium ions coordinate preferentially with
the negatively charged NBOs, there are not enough NBOs to satisfy
the preferred coordination geometry of the sodium ions unless the
NBOs are shared between these ions. This sharing leads to the
relatively short Na—Na nearest-neighbour distance that is observed
here and in previous studies (Hoppe et al., 2000; Pickup et al., 2007).

6. Application to diffraction data from a sol–gel-derived
TiO_2–SiO_2 glass

Titania–silica mixed oxide glasses have properties that are useful for a
number of applications. Such examples are as ultra-low thermal
expansion glasses (Scherer & Brinker, 1990), thin films with tailored
refractive indices (Schultz & Smyth, 1972) and catalysts (Davis & Liu,
1997; Imamura et al., 1995; Holland et al., 2000; Beck et al., 2001).

The data presented here are from a (TiO_2)_{0.18}(SiO_2)_{0.82} sol–gel
sample that has been heated to 523 K. The diffraction data were
collected as part of a wider neutron diffraction with isotopic substi-
tution study of the titanium environment in sol–gel TiO_2–SiO_2
materials (Pickup, Sowrey, Newport et al., 2004). The sample
preparation and collection of the neutron diffraction data are
described therein. The X-ray diffraction data were again collected on
Station 9.1 at the SRS and analysed in the same manner as the data
described in §5.

Fig. 4 shows the T(r) curves from the (TiO_2)_{0.18}(SiO_2)_{0.82} sol–gel
together with their simulations from NXFit. The output parameters
from the fitting process are given in Table 1. The quality of the fits
shown in Fig. 4 is not as good as that achieved for the melt-quenched

Table 1
Structural parameters obtained from the fitting of the diffraction data using NXFit.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Correlation</th>
<th>R (Å)</th>
<th>N</th>
<th>σ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Na_2O)_0.5(P_2O_5)_0.5 metaphosphate glass</td>
<td>P—NBO</td>
<td>1.48 (1)</td>
<td>1.7 (1)</td>
<td>0.03 (1)</td>
</tr>
<tr>
<td></td>
<td>P—BO</td>
<td>1.61 (1)</td>
<td>1.9 (1)</td>
<td>0.05 (1)</td>
</tr>
<tr>
<td></td>
<td>Na—O</td>
<td>2.36 (1)</td>
<td>5.0 (1)</td>
<td>0.17 (4)</td>
</tr>
<tr>
<td></td>
<td>O—O</td>
<td>2.52 (1)</td>
<td>3.7 (1)</td>
<td>0.08 (1)</td>
</tr>
<tr>
<td></td>
<td>Na—Na</td>
<td>2.89 (1)</td>
<td>2.2 (3)</td>
<td>0.07 (3)</td>
</tr>
<tr>
<td></td>
<td>P—P</td>
<td>2.95 (1)</td>
<td>2.1 (2)</td>
<td>0.10 (1)</td>
</tr>
<tr>
<td></td>
<td>Na—O</td>
<td>3.20 (7)</td>
<td>2.6 (2)</td>
<td>0.19 (2)</td>
</tr>
<tr>
<td>(TiO_2)<em>{0.18}(SiO_2)</em>{0.82} sol–gel</td>
<td>O—H</td>
<td>0.99 (1)</td>
<td>0.2 (1)</td>
<td>0.01 (1)</td>
</tr>
<tr>
<td></td>
<td>C—H</td>
<td>1.21 (1)</td>
<td>1.6 (1)</td>
<td>0.05 (1)</td>
</tr>
<tr>
<td></td>
<td>Si—O</td>
<td>1.61 (1)</td>
<td>3.7 (1)</td>
<td>0.04 (1)</td>
</tr>
<tr>
<td></td>
<td>Ti—O</td>
<td>1.82 (2)</td>
<td>2.5 (7)</td>
<td>0.07 (1)</td>
</tr>
<tr>
<td></td>
<td>Ti—O</td>
<td>2.01 (4)</td>
<td>3.7 (10)</td>
<td>0.13 (2)</td>
</tr>
<tr>
<td></td>
<td>Si—H</td>
<td>2.10 (7)</td>
<td>0.6 (1)</td>
<td>0.22 (3)</td>
</tr>
<tr>
<td></td>
<td>O—O</td>
<td>2.64 (1)</td>
<td>3.6 (1)</td>
<td>0.09 (1)</td>
</tr>
<tr>
<td></td>
<td>O—O</td>
<td>2.94 (3)</td>
<td>1.2 (2)</td>
<td>0.17 (1)</td>
</tr>
<tr>
<td></td>
<td>Si—Si</td>
<td>3.08 (2)</td>
<td>2.0 (10)</td>
<td>0.10 (1)</td>
</tr>
<tr>
<td></td>
<td>Ti—Si</td>
<td>3.13 (4)</td>
<td>2.6 (7)</td>
<td>0.09 (3)</td>
</tr>
<tr>
<td></td>
<td>Ti—Ti</td>
<td>3.15 (6)</td>
<td>3.2 (7)</td>
<td>0.21 (3)</td>
</tr>
</tbody>
</table>

![Figure 3](image.png)

Figure 3
Neutron T(r) from (Na_2O)_0.5(P_2O_5)_0.5 metaphosphate glass in the region of the P—O correlation showing the contributions from P—NBO bonds at 1.49 Å and P—BO bonds at 1.61 Å.
sodium metaphosphate glass. This is due to the complexity of sol–gel glasses compared with simple oxide glasses. Sol–gel materials such as the one studied here contain carbon and hydrogen in addition to their oxide components, and their composition can change over time as they age; this makes it difficult to correct diffraction data. The low-r regions (r < 0.8 Å) of the curves in Fig. 4 are not flat, indicating that the corrections to the data have not worked as well as they have for the data shown in Fig. 2. Furthermore, it is known that TiO2–SiO2 sol–gel glasses can reversibly absorb moisture (Mountjoy et al., 1999). Since the neutron diffraction data were collected under vacuum whereas the X-ray data were collected at ambient pressure, there remains the possibility that the low pressure could have partially dehydrated the sample during the neutron diffraction measurement, resulting in an altered composition. Despite these limitations, the key features of the structure of sol–gel (TiO2)0.18(SiO2)0.82 can be obtained from the data in Fig. 4. The Si–O coordination number is close to 4, as expected for a silicate-based material consisting of a network of SiO4 tetrahedra (Wright, 1994). Two Ti–O distances are observed, at 1.82 and 2.01 Å, respectively, with an overall Ti–O coordination number of 6. In agreement with previous studies (Mountjoy et al., 1999; Pickup, Sowrey, Newport et al., 2004), these results are consistent with titanium predominantly occupying a distorted octahedral environment with two short Ti–O and four long Ti–O bonds. The nearest-neighbour O–O and Si–Si distances of 2.64 and 3.08 Å, respectively, are typical of those found in vitreous silica (Wright, 1994). In a fully densified SiO2 network, the O–O and Si–Si coordination numbers are 6 and 4, respectively. Here those numbers are 3.6 and 2.0, reflecting the fact that the sol–gel is only a partially condensed silica network, which is further disrupted by the presence of TiO2. A second O–O distance is also observed, at 2.94 Å, and is assigned to an O–O distance associated with TiO2 polyhedra (Pickup, Sowrey, Newport et al., 2004). The large value of σ for this correlation, of 0.17 Å, reflects the high degree of disorder associated with the titanium environment. The Ti–Ti distance of 3.15 Å observed here agrees well with that determined for a sample with the same Ti/Si ratio but heat treated to 1023 K (Pickup, Sowrey, Drake et al., 2004). In order to achieve a satisfactory fit to the neutron data, it was necessary to include O–H, C–H and Si–OH correlations, providing further evidence that the structure is not fully consolidated after heating to 523 K. Note that these correlations have little effect on the fit to the X-ray data because hydrogen is such a weak scatterer of X-rays.

7. Application of NXFit to the study of other materials

Other examples of the utilization of NXFit in the analysis of diffraction data from a wide range of materials can be found in the literature. Examples of such materials include bioactive glasses (Martin et al., 2012; Smith, Martin et al., 2013), Ca–Mg–Cu metallic glasses (Barney et al., 2011) and amorphous iron phosphate (Al-Hasni et al., 2013).

8. Conclusions

NXFit is a program capable of simulating the pair-distribution functions from amorphous materials. Partial correlation functions are generated in Q space, summed and Fourier transformed to T(r) for comparison with the experimental data in r space. Coordination numbers, atomic separations and disorder parameters are all varied (within user-defined limits) until a satisfactory fit to the experimental data has been obtained. When fitting both neutron and X-ray data simultaneously it is possible to weight one data set relative to the other. The application of NXFit to the fitting of neutron and X-ray data from a melt-quenched (Na2O)0.5(P2O5)0.5 glass and (TiO2)0.18– (SiO2)0.82 sol–gel has been demonstrated here.

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References


Figure 4

Real-space pair-distribution functions (solid lines) together with their simulations (dashed lines) from (TiO2)0.16(SiO2)0.84 sol–gel: (a) X-ray diffraction data and (b) neutron diffraction data. During the fitting process, the relative weightings of the X-ray and neutron data were 0.4 and 0.6, respectively.


