A Structural Study of Praseodymium Gallate Glasses by Combined Neutron Diffraction, Molecular Dynamics and EXAFS techniques.

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Abstract. Neutron diffraction and Extended X-ray Absorption Fine Structure (EXAFS) studies have been carried out on a range of praseodymium gallate glasses (Pr$_2$O$_3$-Ga$_2$O$_3$) prepared by aerodynamic levitation and laser heating. The short and intermediate range ordering around the rare-earth have been obtained by a multi-technique method. The results show that simple molecular dynamics simulations give a good representation of the coordination structure around the rare-earth in these glasses.

1. Introduction.
In recent years there has been great interest in rare-earth doped glasses primarily for their optical properties and applications as laser host materials, phosphors and other optical applications. The optical activity of the ion in the host glass is strongly influenced by the local and intermediate range order, its oxidation state, the quenching rate and the annealing of the glass produced. Hence, in order to understand these materials better and to control and design their properties it is important that good structural models of the glasses can be obtained.

In recent years several techniques have been developed to obtain structural models of glasses from diffraction data. These include the Reverse Monte Carlo (RMC)[1] and Empirical Potential Structure Refinement (EPSR)[2]. However, the former is very sensitive to the starting configuration of the initial model while the convergence of the latter may be strongly influenced by the starting values for the empirical potential (such as the charges on the ions).

An alternative approach to the problem is to use Monte Carlo or Molecular Dynamics simulation techniques[3] to produce distribution functions or diffraction patterns that can be compared directly with the experimental data. However, simple techniques based on pair potentials generally fail to produce good agreement due to absence of explicit three body potentials that are needed to accurately reproduce for example, tetrahedral units in oxide glasses.

In this paper we attempt to demonstrate, by using combinations of neutron diffraction, EXAFS and Molecular Dynamics techniques, that it is possible to obtain high quality information concerning the rare-earth coordination in rare-earth gallate glasses.

2. Experimental Methods.
Praseodymium gallate glass spheres of Pr$_2$O$_3$(x)Ga$_2$O$_3$(1-x) with $x = 0.375$ and diameters of $\sim 3$ mm were produced by aerodynamic levitation and laser heating[4]. Neutron diffraction patterns
Table 1. Parameters used for the Buckingham potential[6]

\[
\phi_{ij} = A_{ij} \exp \left( -\frac{r_{ij}}{\rho_{ij}} \right) - \frac{C_{ij}}{r_{ij}^6} + \frac{q_i q_j}{4\pi\epsilon_0 r} \quad (1)
\]

|        | \(A_{ij}\) (eV) | \(\rho_{ij}\) (Å) | \(C_{ij}\) (eV Å\(^{-6}\)) |
|--------|-----------------|-------------------|-----------------------------|
| \(\text{Pr}^{3+}\)-O\(^{2-}\) | 13431.0          | 0.256             | 0.0                         |
| O\(^{2-}\)-O\(^{2-}\)   | 25.41            | 0.694             | 32.32                       |
| \(\text{Ga}^{3+}\)-O\(^{2-}\) | 2340             | 0.274             | 0.0                         |

were obtained from \(\sim 50\) identical glass spheres placed in the beam on the GEM diffractometer at the ISIS neutron scattering facility at the Rutherford-Appleton Laboratory in the UK. The data were normalised and corrected for self attenuation and multiple scattering using the ISIS GUDRUN software[7].

EXAFS data was collected at the BM29 beamline at the ESRF in Grenoble using finely powdered glass in a Boron Nitride matrix. The EXAFS data were normalised, corrected and analysed with the ATHENA and ARTEMIS programs based on the FEFF7 code. [8, 9]

Molecular Dynamic (MD) simulations of the liquid at 4000K were carried out using the DL_POLY Molecular Dynamics simulation package[5] with Buckingham potentials using the parameters shown in table 1. After equilibration of the liquid the simulation temperature was reduced to 300K and allowed to re-equilibrate. The positions of the atoms in the final configuration of the MD simulation were taken as the starting configuration of a Reverse Monte Carlo refinement [1] of the experimental data. The MD-RMC refinement procedure was carried out using a particle step length of 0.1 Å such that after the refinement was complete no atom had moved more than 0.5 Å from its original position.

3. Results. 
Figure 1 shows the structure factor data [10] obtained from GEM over 8 hours for \(\sim 50\) \(\text{Pr}_3\text{Ga}_5\text{O}_{12}\) glass spheres. Also shown are the corresponding structure factors derived from the MD and MD-RMC configurations.

Figure 1 also shows the transmission EXAFS spectra obtained from the Pr-edge of the glassy sample. It shows the fit using ARTEMIS to the EXAFS spectra obtained from a local cluster model based on the analogue structure of crystalline \(\text{Nd}_3\text{Ga}_5\text{O}_{12}\) that is characterised by a total coordination number of 8 oxygen atoms around the rare-earth ion at three distances (2.14 Å, 2.34 Å and 2.50 Å with coordination numbers of 3, 3 and 2 respectively). This fit is the best of a representative series of such cluster models that were used to attempt to fit the experimental data. Figure 1 also shows the EXAFS signal calculated from the MD and MD-RMC configurations by extracting the individual Pr clusters, calculating the EXAFS signal for the cluster and then averaging the EXAFS signal for all the clusters in the simulation. In this case the cluster size incorporated all the oxygen atoms located within 3.1 Å of the Pr ion.

4. Discussion. 
From figure 1 it can be seen that even before the RMC refinement the EXAFS spectra calculated from the MD simulation is already in close agreement with the observed EXAFS pattern. This
Figure 1. The left-hand figure shows the structure factor \( F(Q) \) (solid line) for Pr\(_3\)Ga\(_5\)O\(_{12}\) measured using the GEM diffractometer at ISIS. The upper curve (+1.5) is the comparison of the data with the \( F(Q) \) calculated from the MD simulation using DL\_POLY (blue dashed line). The lower curve is the comparison of the data with the \( F(Q) \) determined from the MD-RMC refinement (red dashed line). The right-hand figure shows the EXAFS data \( k\chi(k) \). The experimental data is shown as the solid line. The lower curve is a fit using ARTEMIS allowing three separate distances and coordination number of 8 (green dashed line). The middle curve (shifted +0.2) shows the EXAFS signal compared to that predicted from the Molecular Dynamics simulation (blue dot dashed line). The upper curve (shifted +0.4) shows the EXAFS signal compared to that predicted from the MD-RMC refinement (red dash-dot-dot line).

suggests that despite the limitations of the MD simulation to two body potentials and the relatively poor agreement of the measured structure factor with the MD simulations it appears that the coordination around the Pr ion is reasonably well determined by the simulation. From figure 1 it may seem that after the MD-RMC refinement a good agreement between the diffraction data and the model configuration is produced. However, despite the quite large changes in the model’s diffraction pattern observed after this refinement it may be seen that the agreement between the EXAFS data and the calculated spectra has only slightly improved. This agrees with the observation that the local structure around the Pr is already well reproduced in the original MD and has remained largely unchanged during the refinement procedure.

It therefore appears that the large changes observed after the MD-RMC refinement are associated with the Ga-O glass network structure and specifically the rigidity and ordering of Ga\(_4\)O\(_4\) tetrahedra. Calculation of the coordination number of O around Pr with a cutoff distance of 3.1 Å gives 6.8(1) and 6.7(1) for the MD and MD-RMC configurations respectively. This is lower than the value of 8 used in a local cluster model based on the nearest crystal structure. However, it may be noted that the most likely coordination number in both the MD and MD-RMC structures is 7 although these atoms only account for \( \sim 50\% \) of the Pr ions in the simulation. Closer inspection of the configurations reveals that of the rest \( \sim 90\% \) have coordination numbers of either 6 or 8 with the remainder with coordination numbers of 5 and 9. This highlights the difficulty of using a simple cluster refinement to fit the EXAFS data, especially if multiple scattering terms are important. Figure 2 shows representations of the coordination polyhedra obtained from the atom positions in the final MD-RMC refinement. The strong four-fold tetrahedrally coordinated nature of the Ga-O network is clearly observed. In addition it may seen that the structure is dominated by corner shared Ga\(_4\)O\(_4\) tetrahedra with small amount of edge sharing taking place as well. In contrast the Pr-O polyhedra are irregular reflecting the range of coordination numbers obtained in the refinement. The good agreement of the predictions from the MD and MD-RMC models with the EXAFS data suggests that
Figure 2. Coordination polyhedra derived from the final MD-RMC refinement for the Ga-O distribution (left) and the Pr-O distribution (right). The cut-off distances for the bond lengths were taken as 2.1 Å and 3.1 respectively.

basic simulations based on coulomb potentials give a good representation of the rare-earth ion coordination in these glasses.

5. Conclusions.
A neutron diffraction/EXAFS/Molecular Dynamics study has been made for glassy Pr$_3$Ga$_5$O$_{12}$. Analysis of the EXAFS data using cluster models based on crystalline models resulted in relatively poor agreement with the data. In contrast, direct comparison of the EXAFS data predicted from the Molecular Dynamics configurations shows a good agreement suggesting that the simulation is producing a good model of the local structures around the Pr ion. However, comparison of the MD structure to the measured neutron diffraction data showed poor agreement indicating the weakness in the MD model for predicting the Ga-O network structure. Refinement of the MD configuration using a Reverse Monte Carlo method showed considerable improvement in the fit to the diffraction data while maintaining a good agreement with the EXAFS signal. Hence the combination of the three techniques appears to be necessary to obtain optimum atomistic models of the glass. The ability to simultaneously refine the EXAFS data (with multiple scattering terms if necessary) would improve the model further.

6. References.
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