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Structural investigation of gallate glass using L_3-edge extended X-ray absorption spectroscopy and computer simulation

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ABSTRACT

L_3-edge Extended X-ray Absorption Fine Structure (EXAFS) studies have been carried out on a praseodymium gallate glass ($Pr_3Ga_5O_{12}$) prepared by aerodynamic levitation and laser heating. The short range ordering around the rare-earth has been obtained by combined technique including molecular dynamics simulation (MD). The results give an average Pr—O coordination number of 6.68(2) and a mean Ga—O coordination number of 4.29(2). A good agreement between the experimental data and the simple molecular dynamics simulations give rising a glass network of a Pr—O polyhedral structure and a predominant GaO_4 tetrahedral network in this glass.
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1. Introduction

These days there has been great interest in rare-earth gallate glasses primarily for their optical properties and applications as laser host materials, phosphors and other optical applications [1–6]. In particularly, gallate glasses have relatively low vibrational frequencies by comparison with their halide counterparts [4,7]. Consequently, these gallate glasses are of interest as the host glassy matrix for rare-earth atoms such as Pr, Nd, Ho, etc. [3,5,8]. Furthermore, the optical activity of the ions in the host glass is strongly influenced by local and intermediate range order of glassy networks [1–8]. Hence, in order to understand these glassy materials better and to control and design their properties it is very important that good structural models of the glasses can be obtained.

X-ray absorption spectroscopy (XAS) including extended X-ray absorption fine structure (EXAFS) is a powerful technique which can be used to provided the local-structural information around the probing elements in materials especially in glasses. To the best of our knowledge, several techniques such as Reverse Monte Carlo (RMC) [9] and Empirical Potential Structural Refinement (EPSR) [10] have been recently developed to obtain structural models of glasses from diffraction data. An alternative approach to the gallate glasses is to use Molecular Dynamics (MD) simulation techniques [11,12] to produce distribution function or diffraction patterns that can be compared directly with the experimental data.

In this paper we attempt to demonstrate, by using combinations of EXAFS and Molecular Dynamics techniques, that it is possible to obtain high quality information concerning the Pr—O and Ga—O coordinations in the praseodymium gallate glasses.

2. Experimental methods

The praseodymium gallate glass samples were produced from high purity (99.99%) of Pr_6O_{11} and Ga_2O_3 powders. Prior to use, these such starting powders had been calcined in air at 1200 °C for approximately 24 h in order to remove water and any CO_2. Then, pellets of mixed powdered oxides were prepared before melting with a glass composition of $Pr_3Ga_5O_{12}$. Each pellet was melted by heating to approximately 2400 °C using an aerodynamic levitation and laser heating system with argon (99.999%) as the levitation gas [13]. Finally, glass spheres of $Pr_3Ga_5O_{12}$ with diameters of ~2 mm were obtained with their green colour. This green colour shows an existence of Pr^{3+} in produced glasses.

EXAFS spectra for the Pr L_3-edge and Ga K-edge were acquired at the SUT-NANOTEC-SLRI XAS Beamline (BL 5.2) and the BL8 (electron energy of 1.2 GeV; bending magnet; beam current 80–150 mA; 1.1 to 1.7×10^{11} photon s^{-1}) at the Synchrotron Light Research Institute (SLRI), Nakhon Ratchasima, Thailand. To measure EXAFS spectra, the glass spheres will be ground and mixed with BN for a pellet prior to the measurement. The EXAFS spectra were collected in the transmission mode using a Ge (220) double crystal monochromator with an energy resolution ($\Delta E/E$) of 2×10^{-4}. All measured EXAFS spectra were normalized, corrected and analyzed with the ATHENA program [14].

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Table 1
Parameters used for the Buckingham potential.

$\varnothing_{ij} = A_{ij}\ , \exp(\frac{-r_{ij}}{\rho_{ij}}) - \frac{C_{ij}}{r_{ij}^6} + \frac{q_i q_j}{4\pi\epsilon_0 r}$

	A_{ij} (eV)	P_{ij} $(A°)$	C_{ij} $(eV{\cdot}A^{o-6})$
Pr^{3+}—O^{2-}	13,431	0.256	0.0
O^{2}—O^{2-}	25.41	0.694	32.32
Ga^{3+}—O^{2-}	2340	0.274	0.0

Molecular Dynamics (MD) simulations were carried out for praseodymium gallate glasses using the DLPOLY Molecular Dynamics simulation package with Buckingham potentials [15,16]. The used parameters for the Buckingham potential were shown in Table 1. The simulation box was a cube of 29.55 Å which contained 300 Pr, 500 Ga and 1200 O atoms, corresponding to an atomic number density of 0.076 $Å^{-3}$ obtained from the measured sample density of 6.11 g cm^{-3}. The simulations carried out using an NVT Berendsen thermostat. The MD simulation run was started at 2400 K and ran with a time step of 0.001 ps. The system was equilibrated for 1000 steps and then run for an additional 50,000 steps. After this, the simulation temperature was set to 298 K and the process repeated. The final configuration was saved as the starting configuration for the MD-EXAFS calculation.

The MD-EXAFS calculations at Pr L_3-edge and Ga K-edge were calculated using FEFF 8.2 program [17] from the final MD configuration. Individual Pr and Ga clusters were extracted from the MD configuration with the cutoff distances determined by the observed minimum in pair distribution function, gPrO(r) and gGaO(r), respectively. The values of amplitude reduction, S_0^2, and the Debye-Waller factor were set to be 1 and 0, respectively. Unlike conventional EXAFS analysis with first shell fit e.g. crystalline system, the disorder in glass structure is typically calculated through the average of all EXAFS from each different cluster. In this calculation, an average of MD-EXAFS calculated using 300 Pr and 500 Ga clusters is employed in order to obtain a good convergence. Hence, a Debye-Waller term is not necessary in the calculation. Similarly, higher cumulant terms are not included in the MD-EXAFS calculations (Fig. 1).

3. Results and discussion

Fig. 2 shows the pair distribution function, $g(r)$, of the $Pr_3Ga_5O_{12}$ glass sample obtained from the final MD simulations as described so far. From the $g(r)$, it can clearly see a first sharp peak with a tail contribution for each pair distribution function. This distribution pattern exhibits the signature of $g(r)$ of real glass sample unlike crystalline or solid samples in which periodic oscillations with high intensity will be existed after the first sharp peak.

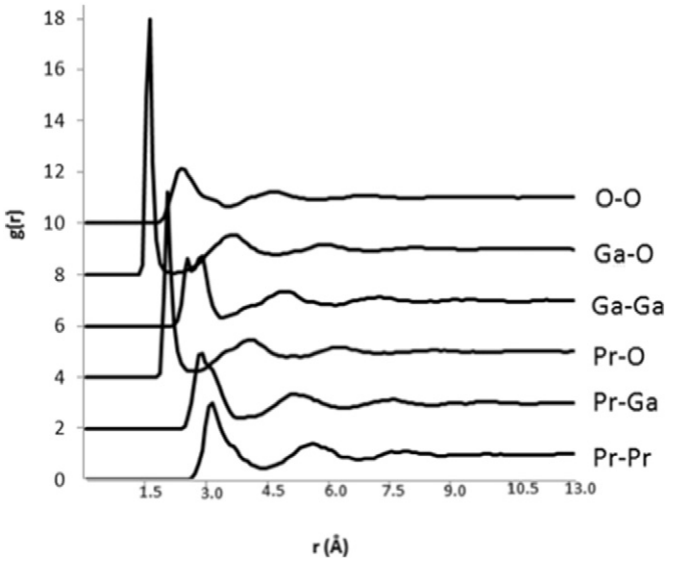

Fig. 2. Partial distribution function of all pair atoms of the $Pr_3Ga_5O_{12}$ glass sample obtained from the final MD simulations.

Fig. 3 shows the measured transmission EXAFS spectra (black circles) obtained from the Pr L_3-edge EXAFS (top) and Ga K-edge EXAFS (bottom) of the $Pr_3Ga_5O_{12}$ glass sample. Again, Fig. 3 also shows a comparison of the calculated MD-EXAFS signal from the final MD configurations (red line) with the measured spectra. Regarding to the MD-EXAFS calculation as reported in the previous section, the cluster size incorporated all the oxygen atoms located within 3.10 Å and 2.30 Å for the Pr and Ga ions, respectively.

From Figs. 3 and 4, by comparison, it can be seen that the EXAFS spectra calculated from the MD simulation are already in close agreement with the observed EXAFS pattern in both k-space and r-space. This suggests that despite the limitations of the MD simulation to two body potentials it appears that coordinations around the Pr and Ga ions are reasonable well determined by simulation. In addition, in Fig.

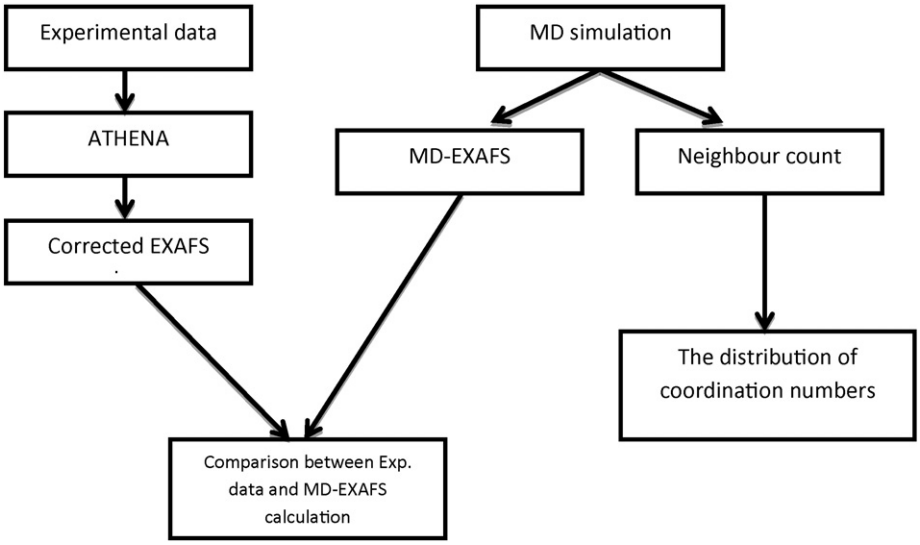

Fig. 1. A flow chart of the programs employed in the EXAFS analysis.

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