Atomistic simulation of densified amorphous alumina

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Recibido el 18 de enero de 2001; aceptado el 18 de julio del 2001

We investigate pressure–induced structural transformation in Al₂O₃ glass using Molecular Dynamics (MD). A detailed analysis of the interatomic distances reveals that as the density increases from 3.175 to 4.2 g/cm³, the Al–O bond length increases, the peak of Al–O coordination number changes from 4 to 6, and the O–Al–O bond angle changes from 105° to 90°. These results provide firm evidence of a structural transition from tetrahedral to octahedral network. According to our simulation, this pressure–induced coordination changes occur at pressures between 15 to 25 GPa.

Keywords: Molecular dynamics, amorphous alumina.

Investigamos, mediante Dinámica Molecular, los cambios estructurales sufridos por el Al₂O₃ amorfo cuando es sometido a presión. Un análisis detallado de las distancias interatómicas revela que al aumentar la densidad desde 3.175 g/cm³ a 4.2 g/cm³, la longitud del enlace Al–O aumenta, el máximo en el número de coordinación Al–O varía de 4 a 6, y el ángulo O–Al–O disminuye de 105° a 90°. Estos resultados constituyen firme evidencia respecto de una transición estructural desde una red tetra a una octaédrica. Nuestra simulación predice que este cambio estructural ocurrirá a una presión entre los 15 a 25 GPa.

Descriptores: Dinámica molecular, alumina amorfa.

PACS: 61.43-j, 61.43.Fs, 81.05.Pj

Aluminum oxide(Al₂O₃) is an important ceramic material whose structure and properties of its liquid and amorphous phases are still poorly understood. For example, amorphous Al₂O₃ is found on the surface of most crystal alumina poly- morph and atomic–level information about its structure under pressure would be an important step in the understanding of the mechanism of the oxidation and passivation processes [1]. In geosciences, aluminosilicates play an important role, and knowledge of their glass and liquids structure under pressure is essential to understand the magma flow at depth [2]. The study of the structure of their terminal phases, SiO₂ and Al₂O₃, offers some insight to this end.

Here we report on results of a MD simulation study of the influence of pressure on the structural correlations of amorphous Al₂O₃. These simulations were carried out for systems at normal mass density ρ₀ = 3.175 g/cm³, and at pressures 0.05, 5.8, 15.3 and 27.3 GPa, corresponding to densities ρ = 3.3, 3.6, 3.9 and 4.2 g/cm³, respectively. MD simulations were carried out in the micro-canonical ensemble (⁴⁰NVE) for 360 Al₂O₃ units, using periodic boundary conditions. The interatomic interactions are represented by a pairwise potential which comprised Coulomb, van der Waals and repulsion energy terms [3], and has been shown to reproduce a number of experimental crystals [4], liquid and amorphous properties [5]. The calculations were done using the program MOLDY [6], with a time step Δt = 1 × 10⁻¹⁶ s.

The amorphous states were prepared by quenching a well equilibrated low density liquid (ρ=2.75 gr/cm³) at high temperature (5000 K). From this liquid alumina, five systems were prepared by simultaneously reducing the lengths of the MD cell and the position of all the atoms. From this stage we thermalized the systems at 3000 K and then lower the temperature to 650 K during the next 200000 time steps. Equilibrium configurations obtained from MD simulations are employed to calculate different kinds of positional and angular properties, by performing an average over 100 uncorrelated configurations.

Figure 1 shows the MD results for the partial and total pair distribution function at three different densities. The Al–Al first peak splits into two peaks when the density increases from normal density (3.175 g/cm³) to 4.2 g/cm³, and the main of these peaks is located at 2.71 Å, close to the nearest neighbor (nn) Al–Al in α–alumina. In a similar way, the O–O nn distance decrease from 2.8 Å at normal density to 2.62 at the highest density. The inverse trend is found for the Al–O bond length which increases from 1.76 to 1.79 Å as the density increases.

Figure 2 shows histograms with the distribution of Al–O coordination numbers at five different densities. We can see that at normal density, more than 75% of Al atoms have tetrahedral coordination and only less than 3% have coordination 6. On the other hand, at the density of 4.2 g/cm³, most Al atoms (64%) have octahedral coordination, whereas only 15% have coordination 4. According to Fig. 2, the transition from the low coordination state to a high coordination state corresponds to a density between 3.6–3.9 g/cm³.

Further information about the local structural units is provided by the angle distribution. In Fig. 3 we display the
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MD results for O–Al–O and Al–O–Al bond angle distributions at three different densities. At normal density, the O–Al–O bond angle has a peak at 104°. Thus, by combining this piece of information with the interatomic distance and the coordination numbers, we conclude that the elementary unit of the system mainly consists of a slightly distorted tetrahedron [7]. As the density increases, this peak shifts to the left, reaching 90° at 4.2 g/cm³. This value is consistent with the changes in the interatomic distances and coordination numbers, the basic units becoming an octahedron. The connectivity of these basic units is described by the Al–O–Al bond angle distribution. At normal density it shows a small peak at 90° and a main peak at 120°, which represents two principal ways of how the tetrahedra are linked each other: edge-sharing tetrahedra and corner-sharing tetrahedra. As the density increases, the small peak at 90° increases, and the large peak at 120° decreases, changing the system from a mainly corner-sharing tetrahedra network at low density to a network which contains mainly octahedra as basic units, linked each other by sharing edges.

In summary, we have reported MD simulation for amorphous Al₂O₃ at five densities and at 600 K. From our results we conclude that an increment of 32 % in density produces dramatic change at the intermediate and short range order, where a structural transformation occurs from a basically AlO₄ corner-sharing tetrahedral network at low density to an AlO₆ edge-sharing octahedral network at high density. According to our simulation, this structural transformation takes place at a pressure between 15–25 GPa.
Acknowledgments

Partially supported by Faculty of Science and Technology, Uppsala University, Sweden and Proyecto Milenio ICM P99–135F “Física de la Materia Condensada”, Chile. Part of the calculations were performed on the CRAY T3E of the National Supercomputer Center in Linköping, Sweden.

7. It is wellknown that for an ideal tetrahedron the O–Al–O bond angle is $\cos^{-1}(-1/3) = 109.47^\circ$. 