AMORPHOUS MATERIALS: PROPERTIES, STRUCTURE, AND DURABILITY†

Atomic structure and transport properties of MgO-Al₂O₃ melts: A molecular dynamics simulation study

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ABSTRACT

Refractory oxide melts of the binary system MgO-Al₂O₃ have been studied by molecular dynamics simulation using an advanced ionic interaction model derived from first-principles. The simulations reproduce well experimental densities, structure factors, and transport properties. Anomalous behavior of the latter was observed as a function of melt composition. The minimum in the Al self-diffusion and the respective maximum in the shear viscosity around MgAl₄O₇ composition are explained by structural changes in the melt.

Keywords: Molecular dynamics simulation, Al₂O₃, MgO, melt, structure, viscosity, diffusion

INTRODUCTION

The prediction of melt properties over a wide range of chemical compositions, pressures, and temperatures is one of the challenges in geomaterials research. The physical properties of different materials are closely related to the structural arrangement of the constituent particles (atoms, ions, molecules) and their chemical interactions. Whereas crystal structures are characterized by a well-defined long-range ordering of particles, which is preserved over a specific range of thermodynamic conditions, the atomic structure in melts only shows short-range order up to a few neighbor distances. Furthermore, melt structures quickly adapt to changing conditions, for instance to changes in pressure and temperature.

A systematic understanding of the relationship between atomic structure and physical properties of interest (density, viscoelastic behavior, ionic and thermal conductivity) may be obtained by combining different experimental techniques (diffraction, spectroscopy, viscometry, etc.). The experimental data are then used to derive empirical models. In this spirit, much experimental data have been collected for silicate melts at ambient pressure (for recent reviews see e.g., Stebbins et al. 1995; Mysen and Richet 2005). However, experiments become much more difficult at the extreme conditions of pressure and temperature. Realistic modeling, however, requires an accurate representation of the particle interactions and sufficient computing power. Very accurate but computationally expensive methods, such as ab-initio molecular dynamics simulations are still restricted to relatively small simulation cells of a few hundred particles. Recently, they were successfully employed to study structural changes in oxide and silicate melts as a function of pressure (Stixrude and Karki 2005; Karki et al. 2006; Wan et al. 2007), but for a reliable calculation of the respective transport coefficients (viscosity, self-diffusivity), larger simulation cells and longer simulation times are needed. Classical interaction models (pair potentials) allow larger scale modeling with thousands to millions of particles. However, their applicability is usually constrained to a limited range of composition, pressure and temperature.

Simple pair potentials usually do not consider instantaneous changes in the electronic structure of a particle due to the interaction with neighboring particles. Such models may be able to reproduce densities and some structural and thermodynamic properties in a range of melt compositions (Matsui 1996; Guillot and Sator 2007) but fail, for example, to describe the vibrational dynamics as sampled by infrared absorption spectroscopy (Wil-