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The structure of Y- and La-bearing aluminosilicate glasses and melts: A combined molecular dynamics and diffraction study

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ABSTRACT

To understand the behavior of rare earth elements (REE) in magmatic systems it is important to characterize in a systematic way their incorporation into silicate melts and glasses. Here, we study the structural environment of the REE Y and La in four aluminosilicate glasses and melts with varying REE content, using a combined simulation and diffraction approach. Glasses are investigated by X-ray and neutron diffraction as well as classical molecular dynamics simulations using two different polarizable ion potentials. Structure models of the corresponding melts are derived from classical and first-principles molecular dynamics simulations. We discuss the effect of temperature on coordination numbers and rationalize the structural changes in response to variations in melt/glass composition in terms of cation field strengths. We find robust evidence that REE and Al coordination numbers decrease with increasing REE content in the investigated melts and glasses. Comparing the two classical potentials, one of them is able to reproduce features of the experimental structure factors with a mixture of corner- and edge-sharing Al-O/REE-O polyhedra, whereas the other potential predicts corner-sharing Al-O/REE-O polyhedra only.

1. Introduction

Rare earth elements (REE) are widely used as geochemical tracers of magmatic processes and thus, their structural incorporation in silicates is of interest for the development of predictive geochemical models. Alkali and alkaline earth bearing (alumino)silicate glasses and melts have been studied extensively, due to their broad range of technological applications and their importance in geoscience. Hence, their structure and properties are relatively well understood (Stebbins et al., 1995; Mysen and Richet, 2005). On the other hand, aluminosilicates containing rare earth elements (REE) are less well studied but have recently attracted considerable interest owing to their remarkable properties and their use in various applications. They exhibit high glass transition temperatures, hardness and refractive indices as well as moderate thermal expansion coefficients (Shelby and Kohli, 1990; Iftekhar et al., 2011). REE-bearing aluminosilicate glasses have been proposed for optical devices (Kohli and Shelby, 1991; Tanabe, 1999). Since rare-earth elements represent analogs for actinides, these glasses have also been studied for applications in nuclear waste storage, and high corrosion resistance in the presence of aqueous fluids was found (Bois et al., 2002).

REE-bearing aluminosilicate glasses have been investigated by a range of experimental techniques, including nuclear magnetic resonance (NMR) (Schaller and Stebbins, 1998; Clayden et al., 1999; Marchi et al., 2005; Florian et al., 2007; Iftekhar et al., 2011, 2009), infrared spectroscopy (Clayden et al., 1999; Marchi et al., 2005) as well as neutron and X-ray diffraction (Wilding et al., 2002; Pozdnyakova et al., 2008). These techniques provide valuable insight into the local atomic structure of glasses such as coordination environments of the probed elements, glass network structures and vibrational properties. Often, the interpretation of experimental data relies on more or less heuristic assumptions about the atomic structure of the probed material. For instance, Iftekhar et al. (2009) fitted

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a structural model to the measured NMR peak shifts and were able to extract information about the glass network connectivity from ^{29}Si signals alone. Another example is the interpretation of X-ray and neutron diffraction data: a common approach to obtain bond lengths and coordination numbers is to fit Gaussian peaks to the Fourier-transformed structure factor, i.e. to implicitly assume a specific structural model for the quantitative analysis of experimental data (Wilding et al., 2002; Pozdnyakova et al., 2008).

Molecular dynamics (MD) simulations are a particularly powerful and predictive method to generate three-dimensional structural models for disordered systems (Allen and Tildesley, 1987) and therefore yield information which is not directly accessible experimentally. To date, there are only a few classical MD studies on REE-bearing aluminosilicate glasses and melts: Du (2009) investigated low-silica (<40 mol%) yttrium aluminosilicates, and Iftekhar et al. (2012) performed MD simulations of Y- and Lu-bearing glasses, with compositions containing less than 50 mol% SiO_2. Haigis et al. (2013) used classical MD simulations to investigate structure of Y in (alumino)silicate melts, with different degree of network polymerization. Recently, Jaworski et al. (2012) and Okhotnikov et al. (2013) published results from classical MD simulations on aluminosilicate glasses also containing La.

The simulation of melts and glasses, however, also poses a fundamental challenge to the MD method: all predictions are dependent on the chosen interaction potentials and their applicability for a given set of conditions has to be tested carefully. Moreover, the MD method allows to simulate the motion of the individual atoms in the system over a certain time, and macroscopic quantities are then obtained by averaging over these atomic trajectories. The statistical results are meaningful only to the extent that the phase space available to the system is sufficiently sampled during the simulation, i.e. that all relevant atomic configurations are visited during the MD run. Even for comparatively dynamic systems such as melts, it can be challenging to ensure that a system has reached equilibrium, especially in chemically complex systems such aluminosilicates. The construction of glass structure models from MD simulations that are comparable to real glasses poses an additional challenge as the glass transition temperature depends on the time scale to freeze the liquid. Depending on the interaction model and available computing resources, the maximum simulation times reach from tens of picoseconds to perhaps hundreds of nanoseconds. To address these issues, we used two complementary simulation approaches.

Ab initio or first-principles MD is based on fundamental laws of nature (quantum mechanics) in the form of density functional theory (DFT) (Hohenberg and Kohn, 1964; Kohn and Sham, 1965) and yields a parameter-free description of arbitrary systems of atoms. Although some approximations have to be made for practical purposes, it provides the most reliable description of atomic interactions currently available and highly predictive in many cases. These qualities, however, come at the expense of high computational cost, which limits simulation times to some tens of picoseconds and system sizes to a few hundred atoms at most. For these reasons, we use *ab initio* calculations primarily to gain insight into melt structures.

The *ab initio* simulations are not only expected to provide accurate structural information on melts but also serve as a benchmark for classical MD simulations, which constitute the second approach to modeling melt and glass structures. In the latter case, atomic interactions are described by a classical potential. Classical simulations are much less demanding in terms of computation time, but their accuracy is not warranted and has to be tested carefully. Their computational efficiency allows simulated quenching of the melts to glasses at much lower rates than can be afforded with *ab initio* techniques (though still much faster than in experiments). The resulting glass structures can then be compared to results from neutron and X-ray diffraction experiments, which were performed in this study to provide a reference for the simulations (see below). The classical MD simulations also allow to study the structural changes between the melt and the glass and to assess the often used assumption that glasses are good structural approximates of melts (and vice versa). The potentials for REE-bearing aluminosilicates used here are an extension of already established and well tested sets of advanced polarizable ion potentials (Jahn and Madden, 2007; Haigis et al., 2013). It is desirable to further develop such accurate and transferable classical potentials, as they are a key to investigate complex geological systems such as mantle melts and solid solutions of mineral phases and the behavior of trace elements therein.

Here, we present the results of a combined MD and neutron/X-ray diffraction study on yttrium- and lanthanum-bearing aluminosilicate melts and glasses, REE_2O_3-Al_2O_3-SiO_2 (REE = Y, La), with high silica content (76 mol% SiO_2). We utilize and compare more refined simulation methods than in cited previous work – new polarizable classical interatomic potentials and *ab initio* molecular dynamics – and systematically analyze the effects of interaction potential, temperature and quench rate on melt and glass structures. Keeping the molar fraction of SiO_2 fixed, the REE/Al ratio was varied between 0.09 and 0.5. We investigated the atomic-scale changes in the structure in response to 1) exchanging Y by La, 2) varying the REE content, i.e. the REE/Al ratio, of the system and 3) increasing the complexity of the classical interaction potential. A particular focus lies on the coordination environment of Y and La, as these are difficult to probe by the otherwise rather powerful NMR technique (Dupree et al., 1989; Schaller and Stebbins, 1998) and diffraction experiments (Leydier, 2010).

2. Simulation procedure

2.1. First-principles molecular dynamics for melts

We performed first-principles, Car-Parrinello molecular dynamics simulations using the CPMD code (Car and Parrinello, 1985; Marx and Hutter, 2000) of REE-bearing aluminosilicate melts of four different compositions, $REEAl_{11}Si_{19}O_{56}$ and $REE_4Al_8Si_{19}O_{56}$, where REE stands for either Y or La. Each simulation cell contained 174 atoms and was repeated periodically in space. Assuming that densities of the melt and the respective glass are similar, we chose the dimensions of the simulation cells such as to obtain the experimentally determined density of the respective glass at room temperature, i.e. 2.91 g/cm^3, 2.97 g/cm^3, 2.94 g/cm^3 and 3.09 g/cm^3, respectively (Leydier, 2010).

Interatomic forces were determined within the framework of DFT, and the exchange-correlation functional was evaluated in the local density approximation (LDA). The interaction between ionic cores and valence electrons was described by Troullier-Martins pseudopotentials (Troullier and Martins, 1991). For Y, the semi-core 4s and 4p electrons were treated explicitly as valence electrons, additionally to the 4d and 5s orbitals. Similarly, for La, the semi-core 5s and 5p electrons were treated as valence electrons, additionally to the 5d and 6s orbitals. This allows for electric polarizability of the Y^{3+} and La^{3+} ionic cores. The cutoff for the expansion of the electronic wavefunctions into plane waves was 90 Ry, which was found to be sufficient to give converged results for the average melt structure. The reciprocal space of the simulation cell was sampled at the Gamma point only, which was sufficient to converge the interatomic forces.

The four simulation cells were pre-equilibrated at 3000 K for 50 ps with a classical MD simulation (see Section 2.2) and further equilibrated for 5 ps using DFT. Data were collected from the following production runs of 10 ps to 15 ps duration. For the Car-Parrinello MD, the fictitious mass of the electronic degrees of freedom was 400 a.u., and the equations of motion were solved with a time step of 0.1 fs. The temperature of 3000 K and the kinetic energy of the fictitious