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1 **REVISION 1**

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

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10
11 **Abstract**

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

18
19 Molecular dynamics simulation; Al₂O₃; MgO; melt; structure; viscosity; diffusion

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22 **INTRODUCTION**

23 The prediction of melt properties over a wide range of chemical compositions, pressures, P ,
24 and temperatures, T , is one of the challenges in geomaterials research. The physical
25 properties of different materials are closely related to the structural arrangement of the
26 constituting particles (atoms, ions, molecules) and their chemical interactions. Whereas
27 crystal structures are characterized by a well defined long-range ordering of particles,
28 which is preserved over a specific range of thermodynamic conditions, the atomic structure
29 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 relation 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, viscosimetry, etc.). The experimental data are then used to derive empirical models. In this spirit, a large number of 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 of the Earth's interior. While some structural changes due to pressure may be preserved in pressure and/or temperature quenched glasses and melts (Xue et al., 1991; Allwardt et al., 2005; Shimoda et al., 2005; Mei et al., 2006), dynamic properties generally need to be studied *in situ* (Farber and Williams, 1996; Suzuki et al., 2002; Reid et al., 2003; Behrens and Schulze, 2003). Due to their high melting temperatures, refractory oxide melts are not easily accessible experimentally even at ambient pressure. Only recently, containerless techniques have been developed to study the atomic structure and dynamics of oxide melts (Poe et al., 1993; Krishnan and Price, 2000; Landron et al., 2001; Sinn et al., 2003; Krishnan et al., 2005; Hennet et al., 2007).

Computer simulations have become a powerful complementary approach to study both melt structures and melt properties. Unlike in experiments, structure and properties are *simultaneously* available from the same simulation (Allen and Tildesley, 1987). In addition, simulations can easily be extended to high pressures and high temperatures. 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 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 (Wilson et al., 1996). For ionic materials, many body interactions may be considered by introducing ionic polarization effects and changes of the ionic size and shape depending on the ionic environment. Such *breathing shell* models are shown to be more accurate and transferable than simple pair potentials (Matsui, 1999; Aguado et al., 2003; Blanchard et al., 2005; Madden et al., 2006). Since for multicomponent systems the number of potential parameters is reasonably large, a systematic approach for parameter optimization is desired. An advanced ionic interaction model, the *Aspherical Ion Model* (AIM) (Aguado et al., 2003; Madden et al., 2006), was recently optimized for the CMAS (Ca-Mg-Al-Si-O) system using *ab initio* electronic structure calculations (Jahn and Madden, 2007a). It was shown to represent well various minerals and melts under *P-T* conditions ranging from the Earth's crust to the lower mantle.

Here, this model is used to extend previous studies of Al_2O_3 melt (Jahn et al., 2006; Jahn and Madden, 2007b) to refractory oxide melts of Al_2O_3 -MgO compositions. The quality of the molecular modeling approach using AIM potentials is assessed systematically by increasing the complexity of the melt system. The results presented here are model predictions since no experimental data have been used in the optimization of the AIM. Recent measurements of the atomic structure (Hennet et al., 2007) and dynamics (Pozdnyakova et al., 2007) of Al_2O_3 -MgO melts are used for comparison. We will discuss the structural changes with composition at ambient pressure and constant temperature and their effect on the transport coefficients.

COMPUTATIONAL DETAILS

The AIM interaction model and its parameterization are described elsewhere (Madden

et al., 2006; Jahn and Madden, 2007a). The model takes into account the Coulomb interaction between charged particles, short-ranged repulsion due to the overlap of the charge densities, dispersion, ionic polarization effects and ion shape deformations. The set of AIM potentials used here was parameterized for the Ca-Mg-Al-Si-O system by reference to electronic structure calculations. The model was shown to be accurate and transferable in a wide range of pressures, temperatures and compositions (Jahn and Madden, 2007a). Here, the same set of interatomic potentials is used.

Molecular dynamics simulations are performed at ambient pressure and constant temperature, T , of 2500 K for five different compositions: Al_2O_3 , MgAl_4O_7 , MgAl_2O_4 , $\text{Mg}_3\text{Al}_2\text{O}_6$ and MgO . The respective simulation cells contain 2160, 2064, 1512, 1892 and 1000 ions, i.e. 432, 172, 216, 172 and 500 formula units. System size effects are expected to be small using reasonably large cells, which is confirmed for MgAl_4O_7 melt using a smaller cell with 1296 ions (108 formula units). The temperature was chosen to be close to experimental conditions. MgO melt at 2500 K is deeply undercooled. The respective data are just for reference and should be taken with care. The mass densities of the equilibrated melts at 2500 K decrease from 2.78 g/cm³ of pure Al_2O_3 melt to about 2.71 g/cm³ of MgO melt. Within the error bars the density varies linearly with composition. Recent experimental data on Al_2O_3 melt density yield 2.79 g/cm³ at 2500 K (Glorieux et al., 1999), which demonstrates consistency between our model and experiment.

For the numerical integration of the equation of motion a time step of $\Delta t=1$ fs is used. During equilibration of 50 ps, pressure and temperature are controlled by a Nose-Hoover thermostat coupled to an isotropic barostat (Martyna et al., 1994) that keeps the simulation cell cubic. Then the barostat is switched off and equilibration is continued at constant volume for another 50 ps before the production runs are started. During the production runs in the NVT ensemble (constant number of particles, volume and temperature) lasting at least 150 ps the ionic trajectories (positions and velocities) and the stress tensor of the simulation cell are written out periodically. Coordination numbers are calculated by counting the number of neighbors of an ion within a given cutoff distance respecting periodic boundary conditions and averaging over ions of the same species and over time. Other structural and the transport properties require the calculation of the respective correlation functions, which

will be given below.

RESULTS

Structural properties

The radial distribution function (RDF), $g(r)$, provides information about interatomic distances and the coordination environment (Allen and Tildesley, 1987). The six partials RDFs of MgAl_2O_4 melt, $g_{\alpha\beta}(r)$ ($\alpha, \beta = \text{Mg, Al, O}$), are shown in Figure 1. The nearest neighbor distances are obtained from the positions r of the first peaks of the respective $g_{\alpha\beta}(r)$. As expected the shortest distance is between O and Al (1.76 Å), whereas the Mg-O distance is 1.98 Å. These two distances are essentially unchanged across the whole composition range. Longer distances such as the O-O nearest neighbor or the Al-O second neighbor distances show a continuous change with composition of the melt. As the Mg content increases distances become larger, which is demonstrated for $g_{\text{O-O}}(r)$ (inset of Figure 1).

At the same time, small changes are observed in the coordination of Al and Mg by nearest O ions. While for pure Al_2O_3 melt, the mean Al coordination is 4.41, it decreases slowly with increasing Mg content to 4.27 in $\text{Mg}_3\text{Al}_2\text{O}_6$ melt (see Figure 2). A similar trend is observed for Mg coordination. At low Mg concentration (MgAl_4O_7), the average Mg coordination is 5.18, whereas it is 4.88 in pure MgO melt. The cation coordination of the end member melts is in good agreement with experimental and earlier simulation data. Earlier results on the Al coordination in Al_2O_3 melt range from 4.2 to 4.4 (Florian et al., 1995; Ansell et al., 1997; San Miguel et al., 1998; Gutierrez et al., 2000; Landron et al., 2001; Krishnan et al., 2005; Jahn and Madden, 2007b). ^{27}Al NMR data of MgAl_2O_4 melt show a mean Al coordination that is closer to tetrahedral than to octahedral Al in the corresponding crystalline phase, spinel (Poe et al., 1993). *Ab initio* simulations of MgO melt yield Mg coordinations between 4.5 and 5 at ambient pressure (Karki et al., 2006).

Larger changes are found in the coordination of the O by Al and Mg. Whereas in pure Al_2O_3 melt almost 75 % of the O are surrounded by 3 Al ions, which gives a mean coordination number of 2.94, the coordination number drops to 2.16 at MgAl_2O_4 and 1.42

at $\text{Mg}_3\text{Al}_2\text{O}_6$ composition, respectively. As expected, the oxygen coordination by Mg shows the opposite trend and increases with increasing Mg content. Adding up Al and Mg contributions, the total oxygen coordination increases with Mg content from 2.94 in pure Al_2O_3 melt to 4.88 in pure MgO melt (Figure 2).

Fourier transformation of the partial RDFs yields the partial static structure factors $S_{\alpha\beta}(Q)$:

$$S_{\alpha\beta}(Q) - 1 = 4\pi\rho \int_0^\infty r^2 \frac{\sin Qr}{Qr} (g_{\alpha\beta}(r) - 1) dr \quad (1)$$

with ρ being the number density of the melt. Q is magnitude of the wave vector or equivalently the momentum transfer of a diffraction experiment. The $S_{\alpha\beta}(Q)$ of MgAl_2O_4 melt are shown in Figure 3. The principal peak positions of the different partials are observed between 2.5 and 2.6 $\text{\AA}^{-1}$. The features at smaller Q (around 1.4 $\text{\AA}^{-1}$) indicate the existence of some intermediate range order in the melt, i.e. structural correlations at distances larger than the nearest neighbor distance.

In order to compare the model structure with experiment, the total static structure factors, $S(Q)$, are calculated as sum of partials weighted with the concentrations, c , and the respective neutron or x-ray scattering lengths, $b(Q)$, of the different species:

$$S(Q) = \frac{4\pi}{\sigma} \sum_{\alpha} \sum_{\beta} \sqrt{c_{\alpha} c_{\beta}} b_{\alpha}(Q) b_{\beta}(Q) S_{\alpha\beta}(Q) \quad (2)$$

σ is the total scattering cross-section for neutrons or x-rays. Excellent agreement with experimental data is achieved for both the x-ray and neutron structure factors of Al_2O_3 melt (Krishnan et al., 2005; Jahn and Madden, 2007b) and MgAl_2O_3 melt (Hennet et al., 2007). The latter are shown in Figure 4. Some deviations are observed at small Q between model prediction and neutron diffraction data. Due to the good agreement in the x-ray case, a probable reason for the discrepancy is some additional small angle scattering that does not stem from the bulk sample. Similar effects have been observed in earlier x-ray diffraction data of Al_2O_3 melt (Ansell et al., 1997; Jahn and Madden, 2007b). It is interesting to note that the first peaks in the total structure factors at 2.35 $\text{\AA}^{-1}$ (x-ray) and 2.70 $\text{\AA}^{-1}$ (neutron) do not correspond exactly to any peak in the partials due to cancellation effects from the

superposition of the partials.

Transport coefficients

Self-diffusion coefficients D_s are calculated from the slope of the mean square displacements (MSD) using the Einstein relation (Allen and Tildesley, 1987):

$$2tD_s = \frac{1}{3} \left\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \right\rangle \quad (3)$$

The MSDs are calculated for each individual ion and then averaged over all ions of a species. As shown in Figure 5 for MgAl_2O_4 melt, the slowest ion is the trivalent Al ion followed by the anion. The slope of the Mg MSD is about a factor of two larger than that of O or Al at MgAl_2O_4 composition.

The evolution of the self-diffusion coefficients with melt composition is shown in Figure 6. While in Al_2O_3 melt, Al and O ions have very similar mobility, the anions are much less mobile than the cations in MgO melt. The self-diffusivities of Al ions are almost constant in the whole composition range but there is a shallow minimum between MgAl_4O_7 and MgAl_2O_4 compositions. The oxygen diffusivity varies little for Al_2O_3 -rich melts, but there is a rapid increase of D_s of oxygen with Mg content for MgO-rich compositions.

The shear viscosity η can be obtained independently from D_s via the stress tensor autocorrelation function (Allen and Tildesley, 1987):

$$\eta = \frac{V}{k_B T} \int_0^\infty dt \left\langle \sigma_{\alpha\beta}(t) \sigma_{\alpha\beta}(0) \right\rangle \quad (4)$$

where V is the volume of the simulation cell, k_B is Boltzmann's constant and $\sigma_{\alpha\beta}$ is an off-diagonal element of the stress tensor ($\alpha \neq \beta$ and $\alpha, \beta = x, y, z$). The obtained viscosities are shown in Figure 7. A maximum in the viscosity is observed for MgAl_4O_7 melt, which is in the same composition range as the shallow minimum in the Al self-diffusion coefficient. The lowest viscosity is observed for MgO melt, even though this melt is already substantially supercooled.

The calculated viscosities are in reasonable agreement with experimental data. Viscosity measurements of pure alumina melt give values of the shear viscosity between 25 and

34 mPa·s at 2500 K (Urbain, 1982), which is somewhat larger than the simulation results. The viscosities of the present model are also slightly smaller than those obtained in our previous study of Al_2O_3 melt using an AIM-type potential optimized for Al_2O_3 only (Jahn et al., 2006), which demonstrates that the absolute value of the viscosity from simulation depends in a very sensitive way on the details of the interaction potential. Much better agreement is expected when activation energies, i.e. differential properties, are compared (Jahn et al., 2006). The viscosity maximum in the $\text{MgO-Al}_2\text{O}_3$ melt system at MgAl_4O_7 composition is also obtained in an experimental study after fitting a generalized hydrodynamic model to inelastic x-ray scattering data (Pozdnyakova et al., 2007).

DISCUSSION AND CONCLUSIONS

While Al and Mg are coordinated by six oxygens in the crystalline oxides corundum and periclase, respectively, the coordination numbers are decreased significantly in the melt. This structural change is reflected by a considerable change in bond lengths. In corundum, all Al ions are in octahedral environment with a mean Al-O bond length of about 1.91 Å. This bond length is reduced in the melt to about 1.76 Å, which is consistent with results from diffraction experiments (Ansell et al., 1997). In the melt, Al ions are able to act as network formers in tetrahedral coordination if they are appropriately charge balanced (Mysen and Richet, 2005). However, network formation is not as efficient as in silicates due to the lower charge of the Al ion compared to the Si ion. The stoichiometry of Al_2O_3 does not allow the formation of the same structures as e.g. in SiO_2 . The deficiency in oxygen either requires the formation of triclusters, where three AlO_4 tetrahedra share one oxygen, or Al ions acting as both network formers and network modifiers.

In Figure 2, only the average coordination numbers are shown. Closer inspection reveals that about 60 % of the Al in Al_2O_3 melt are four-fold coordinated, whereas most of the remaining 40 % are in five-fold coordination. A small amount of Al ions are in 3- or 6-fold coordination (2 % and 3 % respectively). The ratio of four to five-fold coordinated Al increases with Mg content from about 3:2 for Al_2O_3 melt to 3:1 at $\text{Mg}_3\text{Al}_2\text{O}_6$ composition.

It is instructive to look at the O-Al-O bond angle distribution of these differently coordinated Al ions (see Figure 8 for MgAl_2O_4 melt). As expected, the distribution of four-

fold coordinated Al has a peak close to the tetrahedral angle (109.5°). On the contrary, peaks of the five- and six-fold coordinated Al appear at bond angles characteristic for octahedral environment (90° and 180°). This result supports the idea of having Al in both network forming (tetrahedral) and network modifying (octahedral) positions. Three-fold coordinated Al form almost planar AlO_3^{3-} species with a peak in the bond angle distribution close to 120° . However, the lifetime of these structures is extremely short, generally shorter or in the order of a single Al-O vibration. They may either appear as transition states during dynamic coordination changes in the melt or as a result of the way coordination numbers are calculated. Due to the large vibration amplitudes at high temperature, overlap between first and second neighbor shells occurs, which is not accounted for by using a fixed cutoff distance. The O-Al-O bond angle distribution of four-fold coordinated Al (inset of Figure 8) shows considerable composition dependence. It is broadened towards pure Al_2O_3 composition with a shoulder around 90° . This indicates the presence of highly distorted species, whereas for MgO-rich compositions the tetrahedra are more regular.

The average Mg coordination is close to five (Figure 2) with considerable proportions of four- and six-fold coordination (each about 20 to 30 %) and small amounts of three- and seven-fold coordination (less than 6 %). The corresponding bond angle distributions O-Mg-O (see Figure 9) are much broader than those of O-Al-O. Due to the longer Mg-O bond distance and weaker Mg-O bond compared to Al-O, the polyhedra are even more distorted with a dynamic distribution of different types. The large vibrational amplitudes at high T and the highly dynamic nature of coordination changes makes it difficult to identify the type of polyhedron in many cases. For five-fold coordinated Mg we find, e.g., trigonal bipyramids, pyramids, but also intermediate structures.

The macroscopic melt properties do not only depend on the cation coordination but also on how the polyhedra are connected. Considering four-fold coordinated aluminum as the dominant network former the connectivity of AlO_4 tetrahedra is studied in more detail. At meta-aluminous composition, MgAl_2O_4 , all Al^{3+} cations are nominally charge-compensated by Mg^{2+} cations, which would allow the formation of a structure with exclusively four-fold coordinated Al connected by bridging oxygens. However, we have already seen above that there is a rather broad distribution of the Al coordination. This also leads to a variety of

oxygen species, as illustrated in Figure 10. At Al-rich compositions, there is a considerable number of triclusters, i.e. oxygens that are bonded to three tetrahedral aluminums. The number of bridging oxygens connecting two tetrahedra has a maximum at MgAl_4O_7 composition, whereas non-bridging oxygens (bonded to only one Al) and free oxygens increase with Mg content. In pure MgO, only free oxygens are present (due to the lack of Al ions). From silicates it is expected that with increasing degree of polymerization, i.e. increasing number of bridging oxygens, the melt becomes more viscous and less diffusive. This is exactly what we observe here. The maximum of the number of bridging oxygens close to MgAl_4O_7 composition correlates well with the minimum of the Al self-diffusivity and with the maximum of the shear viscosity (see Figures 6 and 7).

Looking at the static melt structure, both the total number of Al and the number of AlO_4 tetrahedra per oxygen ion decrease with increasing MgO content of the melt (see Figure 11). It seems somewhat surprising that this should lead to a viscosity maximum or diffusivity minimum at some intermediate composition. However, contrary to SiO_4 tetrahedra in silicate melts that are considered very stable, the Al coordination in the oxide melts studied here is highly dynamic. A quantitative measure of the dynamic coordination change is the lifetime of the AlO_4 tetrahedra, which we evaluate from the particle trajectories. The corresponding decay function describes the fraction of AlO_4 tetrahedra stable over given time intervals (see inset of Figure 11). At time $t = 0$, this fraction is equal to the number of AlO_4 tetrahedra per oxygen in the static case discussed above (see Figure 11). None of the AlO_4 tetrahedra had a lifetime longer than 10 picoseconds. To a good approximation, the decay function is described by a stretched exponential function:

$$A \exp \left[- \left(\frac{t}{\tau} \right)^\beta \right] \quad (5)$$

The respective relaxation time, τ , increases monotonically with MgO content (see figure 11), i.e. the tetrahedra have a longer lifetime towards the MgO-rich side. The stretching parameter β increases slightly with increasing MgO from 0.89 at Al_2O_3 to 1.02 at $\text{Mg}_3\text{Al}_2\text{O}_6$ composition. The reverse behavior of availability of AlO_4 tetrahedra (also expressed by parameter A) and their respective lifetimes as a function of composition

indicates a complex interplay of different structural and dynamic processes that may explain the anomalous behavior of the transport coefficients.

Finally, we discuss the validity of empirical relations between viscosity and diffusivity for the melts studied here. The most prominent models that link the melt viscosity η to a diffusion coefficient D are expressed by the Stokes-Einstein ($D=k_B T/6\pi R\eta$) and the Eyring ($D=k_B T/\lambda\eta$) equations. While the former is derived for Brownian motion of large particles in low viscosity fluids, the latter is usually applied to highly viscous melts. The Stokes-Einstein radius R is the effective radius of a hard sphere that diffuses with the same rate as the diffusing particle in the fluid. The Eyring model assumes that thermally activated jumps control both viscosity and diffusion of the network-forming particles. λ is the respective jump length. Using $\eta = 20$ mPa·s and $D = 1.5 \times 10^{-9}$ m²/s as typical values of the viscosity and O or Al self-diffusivity, respectively (see Figures 6 and 7), yields $R = 0.61$ Å and $\lambda = 11.5$ Å. The obtained jump length is much larger than the interionic distances, which suggests that the Eyring equation is not directly applicable to the oxide melts considered here. This is not surprising since Al is only a weak network former. One could imagine that differently coordinated Al cations diffuse at different rates. However, due to the dynamic changes in coordination at time scales of the MD simulation a separate estimate of diffusion rates of four- and five-fold Al is very difficult. Using the self-diffusivities of tetrahedral Al only could result in a smaller jump length λ . The Stokes-Einstein radius of 0.61 Å is close to the radius of the Al³⁺ ion (0.54 Å) but considerably smaller than the radius of the much larger anion. Larger discrepancies also occur if the Stokes-Einstein relation is applied to the Mg cation. The higher diffusivity leads to a smaller R although the Mg²⁺ is larger (0.72 Å) than the Al³⁺ ion. Hence, we conclude that for MgO-Al₂O₃ melts the direct application of neither the Stokes-Einstein nor the Eyring model gives a fully satisfactory description of the relation between diffusivity and viscosity.

In conclusion, we have presented a model calculation of refractory oxide melts that reproduces almost quantitatively the available experimental data. The simulations provide insight into the relations between the atomic structure and the macroscopic transport properties of these melts. Molecular dynamics simulations are very helpful in this respect, especially at extreme conditions that are difficult to access experimentally. They can also

help to interpret experimental data and to test models of melt properties. Perspectively, we hope to develop and apply similar advanced interaction models to other oxide and silicate melts and to get a systematic understanding of melt properties. Eventually, we would like to *predict* quantitatively properties of melts with natural composition from *first-principles*.

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Figure captions

Figure 1: Partial radial distribution functions of MgAl_2O_4 melt at $T=2500$ K. The inset shows the compositional change of $g_{\text{OO}}(r)$ at constant temperature.

Figure 2: Mean coordination numbers as a function of melt composition. Lines are just a guide to the eye. Extrapolated values are shown by dashed lines.

Figure 3: Partial static structure factors of MgAl_2O_4 melt at $T=2500$ K.

Figure 4: Total static structure factors of MgAl_2O_4 at $T=2500$ K from MD simulation compared to neutron and x-ray diffraction data at $T=2423$ K (Hennet et al., 2007).

Figure 5: Mean square displacements for the MgAl_2O_4 composition at $T=2500$ K.

Figure 6: Composition dependence of the self-diffusion coefficients at $T=2500$ K. The errors are in the order of the symbol size.

Figure 7: Composition dependence of the shear viscosity of $\text{MgO-Al}_2\text{O}_3$ melts at $T=2500$ K.

Figure 8: O-Al-O bond angle distribution in MgAl_2O_4 melt at $T=2500$ K. The inset shows the change of O-Al-O bond angles for four-fold coordinated Al as a function of melt composition.

Figure 9: O-Mg-O bond angle distribution in MgAl_2O_4 melt at $T=2500$ K.

Figure 10: Relative proportions of oxygens connected to four-fold coordinated Al ions. Coordination numbers are zero for free oxygens, one for non-bridging oxygens, two for bridging oxygens and three for tricluster oxygens.

Figure 11: Total number of Al and number of AlO_4 tetrahedra per oxygen ion as a function of melt composition (left axis) and average lifetime τ of AlO_4 tetrahedra from fitting equation 5 (right axis). Inset: Decay function describing the fraction of AlO_4 tetrahedra stable over given time intervals for the different compositions. While at small times the number of tetrahedra is largest for Al_2O_3 melt, their coordination is changed more rapidly than those of MgO-richer compositions.