

Computer modeling of the equations of state of crystals and melts in the CaO-MgO-Al₂O₃-SiO₂ system

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Crystals and melts in the CaO-MgO-Al₂O₃-SiO₂ (CMAS) system are important components of the earth's crust and mantle. Both molecular dynamics (MD) and lattice dynamics (LD) methods are used to calculate the properties of crystals, while the MD technique is applied to simulate melts. The interionic potential is taken to be the sum of pairwise additive Coulomb, van der Waals, and repulsive interactions. In addition, in order to take account of many-body forces in crystals and melts, the breathing shell model (BSM; Matsui, 1998) is developed for simulation, in which the repulsive radii of O ions are allowed to deform isotropically under the effects of other ions in the system concerned. The net charges of the ions are constrained to be $q(\text{Ca}) = q(\text{Mg}) = 2/3q(\text{Al}) = 1/2q(\text{Si}) = -q(\text{O})$ to apply the potential to both crystals and melts with any composition in the CMAS system. Required energy parameters were derived empirically to reproduce the observed temperature-pressure-volume equations of state of a wide structural variety of crystals in the CMAS system, as well as the measured volumes of enstatite, wollastonite, diopside, and anorthite melts at high temperatures.

The LD and MD simulations with the BSM potential are quite successful in reproducing well these measured properties of both crystals and melts. In enstatite, wollastonite, diopside, and anorthite melts at 1900 K and 0 GPa, we found the simulated cation coordination numbers are four for Si, about four, five, and seven for Al, Mg, and Ca, respectively. The pressure dependences of cation coordination numbers in these melts are also investigated. The MD method is further applied to study the compositional dependences of the volumes of melts in the SiO₂-Al₂O₃, SiO₂-Ca₃Al₂O₆, and MgSiO₃-CaSiO₃ joins at high temperatures.

Molecular dynamics simulations of the structural and kinetic properties of amorphous intergranular films in alumina

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Thin, intergranular films (IGFs) of only one to a few nanometers thickness are prevalent in minerals and, while making up only a small volume percent of the material, often strongly influence material properties. However, the glassy nature and thickness of the IGF have made experimental observations of atomistic descriptions of these phases difficult to obtain until recently and computational techniques offer a complementary approach to understanding these atomistic details. The results of molecular dynamics computer simulations of the structural and kinetic properties of glassy calcium aluminosilicate (CAS) intergranular films (IGFs) in polycrystalline alumina will be presented. Calcia and silica can exist as impurities in alumina and segregate out to the crystal surface at high temperatures, affecting dissolution and grain growth. In experimental studies using liquid phase sintering, composition of the IGF was shown to significantly alter grain growth, although the mechanisms were not understood. The role of composition on the atomistic structure of the IGF and growth behavior of different crystallographic orientations will be presented. The simulations show ordering into the amorphous IGF caused by the presence of the crystal interface. Such structural changes also effect diffusion of species within the IGF. The simulations also show that grain growth along the surface normal of the basal plane is inhibited by preferential segregation of Ca ions at the IGF/crystal interface, although this behavior is affected by composition of the IGF. Dissimilar behavior occurs at the prism surface, where Al (and O) adsorption from the IGF onto the prism surface occurs in a manner consistent with grain growth along the surface normal. These simulation results are consistent with experimental studies regarding anisotropic grain growth in alumina as a function of composition and provide atomistic mechanisms regarding grain growth.