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First-principles prediction of pressure-enhanced defect segregation and migration at MgO grain boundaries†

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Abstract

Understanding the ability of grain boundaries to accommodate point defects and enhance diffusion rates in mantle materials represents an important but challenging problem. Extant experimental studies and recent computational efforts are mainly limited to the ambient pressure. Here, we investigate this problem for MgO at the atomistic level by performing first-principles simulations, based on density functional theory, of the {310)}/[001] tilt grain boundary in MgO at pressures up to 100 GPa. Our results show that native defects and impurities (Ca, Al, and proton modeled here) favorably segregate to the boundary, with the segregation considerably increasing with pressure. They also imply that grain boundary diffusion is easier, and more anisotropic and complex than bulk (lattice) diffusion: The calculated migration enthalpies for host ions and impurities at the grain boundary are smaller than the bulk values, more so at higher pressures with their values being as low as ~1.5 eV at 100 GPa compared to the bulk values of ~4 eV. Thus demonstrated high-defect activity of grain boundaries in MgO—a major phase of Earth's lower mantle is expected to be relevant to our understanding of mantle rheology and geochemical process.

Keywords: Grain boundaries, defects and diffusion, high pressure, first-principles computation, MgO, mantle materials