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Proton-containing defects at forsterite {010} tilt grain boundaries and stepped surfaces

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ABSTRACT

Atomistic simulation techniques are used to investigate the effect of proton-containing defects on the structure and stabilities of a range of grain boundaries of forsterite. We study two series of stepped {010} tilt boundaries that are at 90° to each other: one with the {100} plane as step wall and the other with the {001} plane. Each series consist of several grain boundaries with increasing terrace area (i.e., decreasing boundary angle). The ratios of boundary and surface energies γ_b/γ_s and $\gamma_b/\gamma_{\{010\}}$ with boundary angle show maxima at a boundary angle $\phi = \sim 30°$ and minima at $\phi = 0°$ and ~60°. The adhesion energies of the two series show a minimum at low boundary angle ($\phi = 20–30°$), indicating that there is an optimum size for the {010} terrace area, where the relative stabilities of grain boundary and related surface make separation of the boundary into the free surfaces energetically least expensive.

Dissociative adsorption of water molecules in the bulk crystal is preferred at the M2 site, but is an endothermic process with a calculated hydration energy of +119 kJ/mol. Hydration of the grain boundaries on the other hand is energetically favorable with hydration energies tending toward –80 kJ/mol compared with a surface hydration energy at the planar {010} surface of –90 kJ/mol. We also investigated the adsorption of protons at cation defects, by modeling the process of replacement of Mg ions in the bulk and along the grain boundaries by two H^+ ions each. Replacement of Mg^{2+} in the bulk crystal occurs preferentially at the M1 site and is calculated to be exothermic with a replacement energy of –78 kJ/mol; Mg^{2+} replacement along both series of grain boundaries is also an exothermic process. The replacement energies tend to a constant value of approximately –210 kJ/mol with increasing terrace area. (cf., the calculated value for the planar {010} surface of –230.4 kJ/mol).