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Modelling Proton-Containing Defects in Forsterite

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Electronic structure calculations using the density functional theory (DFT) within the generalised-gradient approximation and ultra-soft pseudo-potentials have been used to investigate the absorption of water in forsterite (Mg_2SiO_4), periclase (MgO) and alpha-quartz (SiO_2). The calculated structural parameters of forsterite are found to be in good agreement with experiment. Absorption of water in the perfect lattice is calculated to be an endothermic process in all three materials. Replacing MgO units with water molecules in MgO and forsterite is also energetically unfavourable, although at the M1 site it is only just endothermic. However, replacing SiO_2 units with water molecules in both alpha-SiO_2 and forsterite is calculated to be exothermic and we therefore expect water to be present in these materials mainly as OH clusters at silicon vacancy sites.

Atomistic simulation techniques are employed 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 which are at a 90 degree angle to each other: one with the {100} plane as step wall and the other with the {001} plane. Each series consist of a number of grain boundaries with increasing terrace area (i.e. decreasing boundary angle). The ratios of boundary and surface energies gamma(b)/gamma(s) and gamma(b)/gamma{010} with boundary angle show maxima at a boundary angle of ~30 degrees and minima at 0 and ~60 degrees. The adhesion energies of the two series show a minimum at low boundary angle (20-30 degrees), 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. Hydration of the grain boundaries is calculated to be energetically favourable with hydration energies tending towards -80kJ/mol compared with a surface hydration energy at the planar {010} surface of -90kJ/mol. We also investigated the adsorption of protons at cation defects, by modelling the process of replacement of magnesium ions in the bulk and along the grain boundaries by two H^+ ions each. Replacement of Mg^{2+} ions in the bulk crystal is shown to occur preferentially at the M1 site and is calculated to be exothermic with a replacement energy of -78kJ/mol; magnesium replacement along both series of grain boundaries is also an exothermic process. Again the replacement energies tend to a constant value of approximately -210kJ/mol with increasing terrace area. (cf. the calculated value for the planar {010} surface of -230.4kJ/mol).