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Point defect reactions and hydrogen diffusion in hydrous forsterite from first-principles calculations

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The relative stabilities of various hydrogen-bearing point defects and the mobility of hydrogen in forsterite have been investigated using Density Functional Theory. In particular, energetic barriers separating the lowest energy configurations of two charge-neutral defects $(4H)_{Si}^{X}$ and $(2H)_{Mg}^{X}$ and their respective associate defects following potential dissociation reactions were determined using the Nudged Elastic Band (NEB) method. Dissociation of the $(2H)_{Mg}^{X}$ defect forming $(H)_{Mg}' + H_i^{\bullet}$ is characterised by an activation enthalpy of 1.2 eV whereas the activation enthalpy for the reaction $(4H)_{Si}^{X} \rightarrow (3H)_{Si}' + H_i^{\bullet}$ is 1.5 eV.

The mechanisms for dissociation, as shown by the NEB calculations, involve breaking an OH bond at the neutral defect and formation of a new OH bond at an interstitial site (oxygen bonded to a neighbouring Si). This is found to be coincident with the transition state for dissociation of the $(2H)_{Mg}^{X}$ defect, whereas breakage of the OH bond also occurs at 1.2 eV for the $(4H)_{Si}^{X}$ defect but an additional 0.3 eV is needed to overcome the energy barrier leading to a stable associate defect.

Additional calculations were also performed to examine the mobility of a free proton hopping between interstitial sites, which is likely to be an important means for charge transport in nominally anhydrous silicate minerals. Interstitial H_i species were found to be stable only at the O3 (three configurational species) and O2 (one configurational species) sites, resulting in eight distinct H_i species per SiO_4 unit and numerous intratetrahedral and intertetrahedral hopping pathways available for proton diffusion throughout the lattice. The absence of cation vacancies in these calculations allows for much lower energetic barriers between H_i sites due to longer and weaker OH bonds. This therefore suggests that the dissociation of any H-bearing defect located at a cation vacancy is the rate limiting step in the hydrogen diffusion process and that the observed activation enthalpy for charge transport will be indicative of the dominant H-bearing point defect species in the absence of other more efficient charge transport processes such as polaron or ionic conduction.