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Nudged elastic band calculations of the $(4H)^{X}_{Si}$ hydrogarnet type defect in Mg_2SiO_4 forsterite

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Abstract

First-principles calculations based on density functional theory (DFT) using the generalized gradient approximation (GGA) were performed to assess the energetic barriers separating different topological configurations of the $(4H)^{X}_{Si}$ hydrogarnet type defect in Mg_2SiO_4 forsterite with the climbing image nudged elastic band (CI-NEB) method. Barrier heights are low (<0.6 eV) with respect to typical activation energies observed for H-diffusion but more comparable to those for electrical conductivity of H_2O-bearing nominally anhydrous minerals. As can be expected, hydrogen bonding to O atoms both within the defect and belonging to adjacent tetrahedra plays a fundamental role in the stability of each configuration. Saddle points along the minimum energy path (MEP) typically correspond to the transition of one hydrogen bond breaking to form a new hydrogen bond such that one or more OH bonds have shifted in direction without themselves breaking. MEPs show that slightly out-of-plane torsional hopping from one configuration to another can reduce the height of the barrier. We illustrate several different reaction coordinates between symmetry equivalent pairs of configurations and non-symmetry related pairs that can result in an effective means of local charge transport by shifting the center of mass of the $(4H)^{4+}$ cluster within the defect site without proton transfer to an interstitial site. Especially at low temperatures in the absence of thermally activated processes that result in the breaking of stronger chemical bonds, these types of configurational transformation mechanisms are likely to be important contributors to the dielectric behavior of nominally anhydrous silicate minerals and also affect both electrical conductivity and electrical conductivity anisotropy when investigated by AC methods such as impedance spectroscopy. The NEB method can also be used to examine more effective charge and mass transport processes that involve the dissociation of the hydrogarnet defect into more complex chemical species, which might involve similar hydrogen bond breaking and forming processes observed in this study along with more significant atomic displacements.

Keywords: Nudged elastic band, density functional theory, point defects, hydrous forsterite, nominally anhydrous minerals, hydrogen bonding