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A first-principles investigation of hydrous defects and IR frequencies in forsterite: The case for Si vacancies

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Abstract

We investigate charge-balanced hydrous magnesium and silicon defects [$(2H)^{X}_{Mg}$, $(4H)^{X}_{Si}$] by first principles. Two new lowest-energy hydrogen configurations are proposed for $(4H)^{X}_{Si}$. With these new configurations, the distribution of O-H stretching phonon frequencies in Group I (>3450 cm^{-1}) are better reproduced. Substitution of silicon with four hydrogen atoms gives rise to significant elongation of distances between O atoms at the tetrahedron of the silicon vacancy. Our calculations indicate that the correlation between O-O distances and O-H stretching phonon frequencies, which has been well established for hydrous minerals, does not apply directly to nominally anhydrous minerals and should not be used to determine the identity of hydrous defects responsible for infrared absorption peaks.

Keywords: Hydrous defects, forsterite, phonon frequencies, nominally anhydrous minerals, first principles