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Electronic Supplementary Information

Density functional theory and thermodynamic analysis of the bridgmanite surface structure

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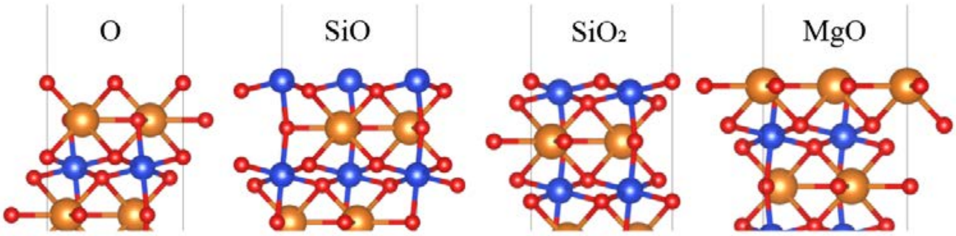
Slab Structures:

The following is the side views of possible surface terminations structures. The red sphere is the O atom, blue sphere is the Si atom and orange sphere represent the Mg atom.

(001)



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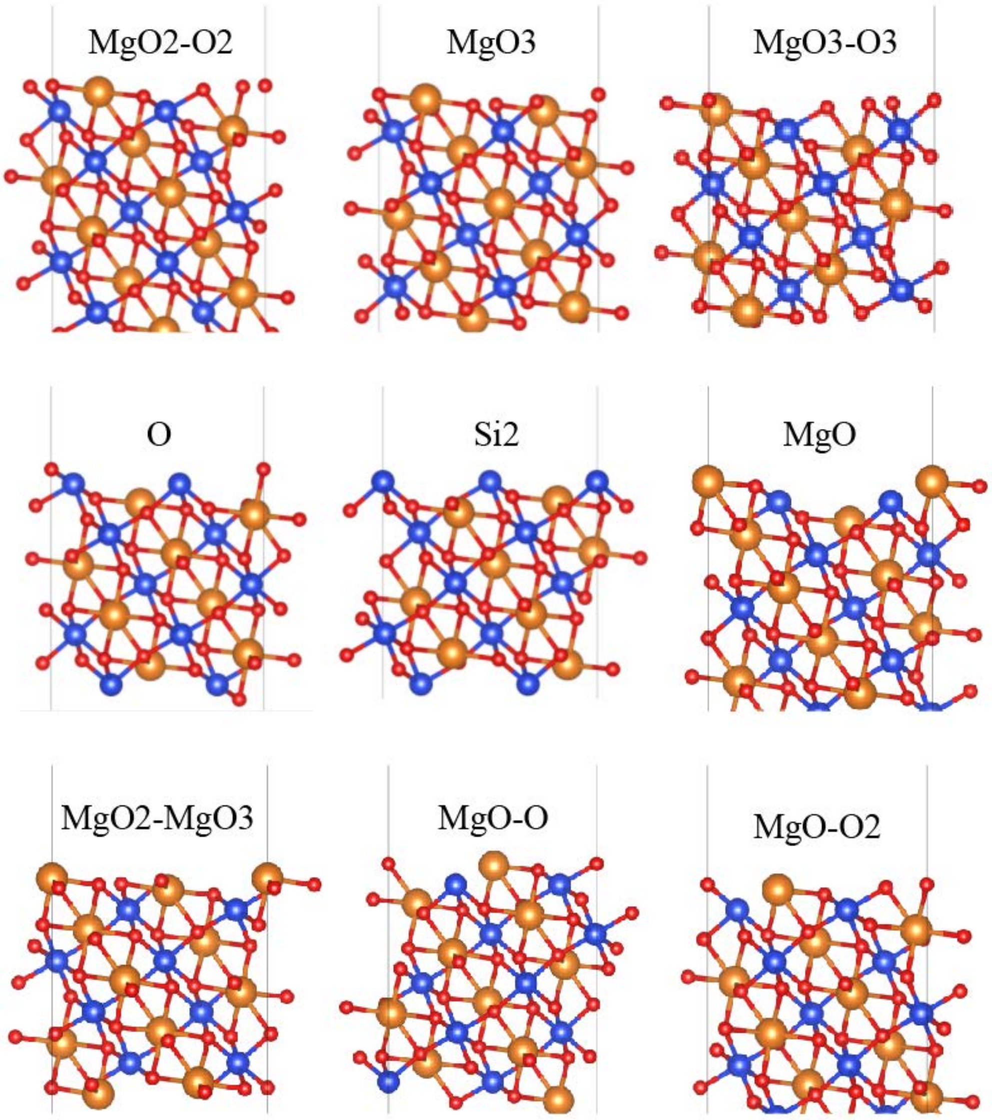

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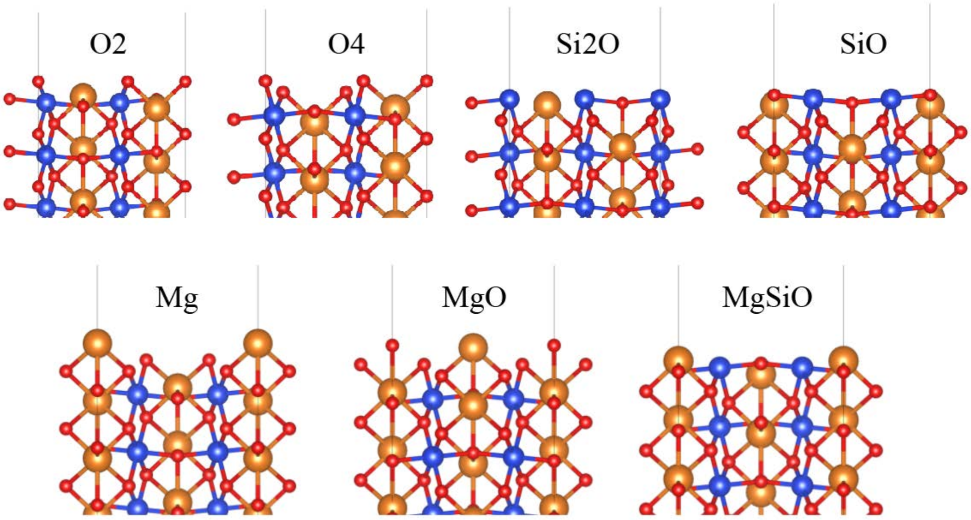

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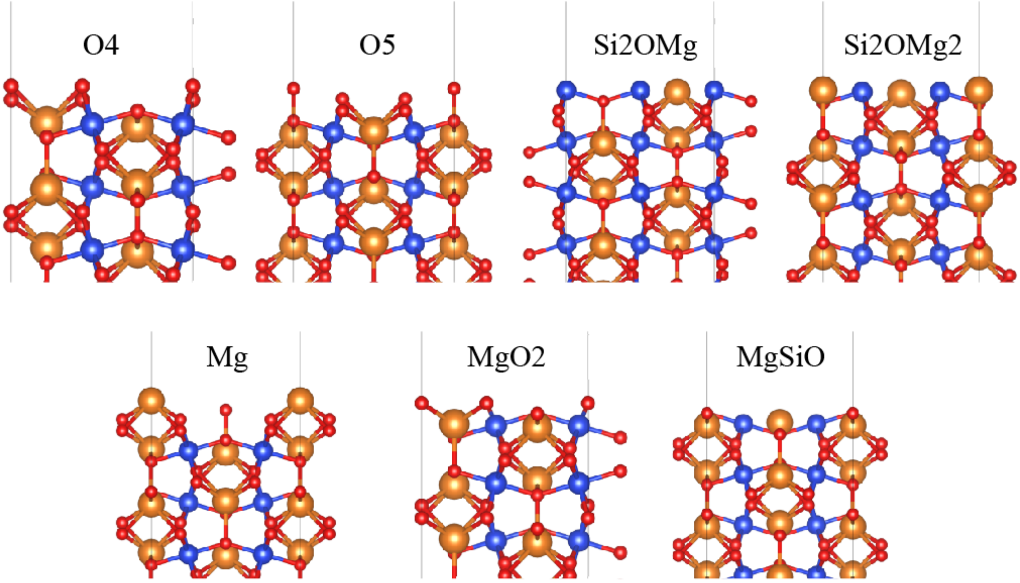

Determination of surface Gibbs free energy:

To determine the stabilities of various surface terminations under ambient conditions (temperature and oxygen partial pressure), the surface Gibbs free energy (Ω) of a specific surface termination of bridgmanite is calculated by:

$$\Omega_i = \frac{1}{2A}\left(G^i_{slab} - N_{Mg}\mu_{Mg} - N_{Si}\mu_{Si} - N_O\mu_O\right) \quad \text{(S1)}$$

where N_{Mg}, N_{Si}, N_O denote the numbers of Mg, Si and O atoms in the slab, G^i_{Slab} is the Gibbs free energy of the symmetric slab with identical surface terminations on both top and bottom sides, and μ_{Mg}, μ_{Si} and μ_O are the chemical potentials for the Mg, Si and O atomic species in the forsterite crystal.

Due to the surface of each slab is equilibrium with bulk bridgmanite, the chemical potential of bridgmanite, μ_{MgSiO_3}, which is equal to the sum of the chemical potentials of all atom types in the $MgSiO_3$ crystal:

$$g_{MgSiO_3} = \mu_{MgSiO_3} = \mu_{Mg} + \mu_{Si} + 3\mu_O \quad \text{(S2)}$$

By introducing deviation of the Mg and Si chemical potentials,

$$\Delta\mu_{Mg} = \mu_{Mg} - g_{Mg}^{bulk} \quad \text{(S3)}$$

and

$$\Delta\mu_{Si} = \mu_{Si} - g_{Si}^{bulk} \quad \text{(S4)}$$

from this we can rewrite the Equation (S5) as:

$$\Delta\mu_{Mg} + \Delta\mu_{Si} + 3\Delta\mu_O = \Delta g_f(MgSiO_3) \quad \text{(S5)}$$

Where $\Delta g_f(MgSiO_3)$ means the Gibbs free energy of formation for $MgSiO_3$ from Mg, Si and O_2 in their standard states.

$$\Delta g_f(MgSiO_3) = g_{MgSiO_3}^{bulk} - g_{Mg}^{bulk} - g_{Si}^{bulk} - \frac{3}{2}E_{O_2} \quad \text{(S6)}$$

We explicitly introduced the vibrational part contribution into the Gibbs free energy. The Gibbs free energy g can be approximated as total energy and F^{vib}:

$$g = E + F^{vib} - TS^{conf} + pV \approx E + F^{vib} \quad \text{(S7)}$$

Here, the terms F^{vib}, T, p, V and S^{conf} correspond to vibrational free energy, temperature, pressure, volume, and configurational entropy, respectively. In addition, TS^{conf} are approximated to be zero due to their negligible energetic contributions, as has been done in previous studies. The crystal volume per molecule is about 14.449 Å^3, We tested pressure caused volume variation is no more than 4% per unitcell from 0.1 to 30 GPa. So the largest pV term is only several 0.037eV up to 30 GPa which can be neglect due to the DFT calculation errors. Thus g in Equation S8 is simplified to contributions from only E and F^{vib}. This F^{vib} term can be expressed using phonon density of states(DOS) as follows:

$$F^{vib} = \frac{1}{2}\sum_{qj} h\omega_{qj} + k_B T \sum_{qj} \ln[1 - \exp(-h\omega_{qj} / k_B T)] \quad \text{(S8)}$$

Where q is the wave vector and j is the band index, ω_{qj} is the phonon frequency of the phonon mode labeled by a set { q, j }. Phonon calculations were conducted based on density functional perturbation theory (DFPT) implemented in VASP software in connection with the Phonopy software[1].

Reference

1. A. Togo and I. Tanaka, ***Scripta Materialia***, 2015,108, 1–5.