**Motivation**

- CaMnO₂ has attracted attention due to its multiferroicity, thermoelectric efficiency, colossal magnetoresistance, and catalytic properties.
- Recently, an experimental study reported that CaMnO₂ acts as an efficient catalyst for water oxidation, but very little is known about the mechanism.
- CaMnO₂ surface plays a significant role in the development and understanding of CaMnO₂ as a potential catalyst.
- Neither experimental nor theoretical studies have investigated the structural composition and reconstructions of CaMnO₂ surfaces under different environmental conditions.

**Computational Methods**

- Density Functional Theory (DFT) calculations were performed within GGA using the Perdew-Burke-Ernzerhof functional for solids (PBEsol).
- Spin-polarized electronic densities are used, treating the magnetic moments collinearly.
- Norm-conserving, optimized, ultrasoft pseudopotentials for all atoms.
- The Brillouin zone was sampled using 4x4x4 Monkhorst-Pack k-point mesh for surface structures.
- Density functional perturbation theory (DFPT) was used to calculate phonon frequencies at the Γ point for all secondary phases.

**CaMnO₂ (001) Surface Structures**

- The structures computed are constructed with (2x2x1) surface symmetry and symmetrical slabs.
- The surface terminations are designed by varying the stoichiometry of Ca, Mn and O including additional CaOₓ and MnO<y layers.
- Each surface termination is identified based on its termination (either CaO or MnO₃) and whether it contains vacancies (\(v\)) or adatoms (\(a\)).

**Thermodynamic Stability**

The surface free energy, \(\Delta F\), of an individual surface slab, \(i\), is defined as the excess amount of free energy needed to create the surface from its bulk form:

\[
\Delta F_i = \frac{1}{2} \sum_{\text{vib.}} \mu_i + \left( \frac{1}{2} \sum_{\text{vib.}} \mu_i + \sum_{\text{vib.}} \mu_i \right) \Delta E_{\text{vib.}}
\]

The following term accounts for the off-stoichiometric atoms of component \(x\) with respect to \(i\) in the slab:

\[
\Gamma_{\text{vib.}} = \frac{1}{2} \left( N_x - N_{x_{\text{vib.}}} \right) \sigma_{\text{vib.}}
\]

Then, Eq. (1) and (2) are merged to rearrange the definition of the Gibbs surface free energy,

\[
\Delta F_i = \frac{1}{2} \sum_{\text{vib.}} \mu_i + \left( \frac{1}{2} \sum_{\text{vib.}} \mu_i + \sum_{\text{vib.}} \mu_i \right) \sigma_{\text{vib.}} \]

In addition, the bulk stability region is defined by a set of boundary conditions that determine the stability range of the chemical potential with the following conditions:

- The Ca and Mn metals are not allowed to lose the bulk and form precipitates.
- The bulk is stable when the metal oxides do not precipitate.
- This criteria accounts for the possible precipitation and arrangement of complex sub-phases from the bulk.

**Surface Phase Diagram**

| Surface Phase Diagram of CaMnO₃ (001) Surface | Thermodynamic Stability of the CaMnO₃ (001) Surface | Temperature Dependence |

**Conclusions**

- A series of CaO and MnO₃ terminated surfaces with different combinations of its components’ vacancies, all atoms and additional layers are reported using all site thermodynamics to theoretically predict the surface phase diagram of CaMnO₃ (001).
- The stability region defined by a criteria of boundary conditions is distinctly dominated by CaMnO₃, CaMnO₂, and CaO.
- The stability region shifts as temperature increases leading to the presence of MnO₃-based surfaces.
- The Surface phase diagram, specifically the MnO₃-terminated surfaces, is sensitive to magnetic ordering.
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