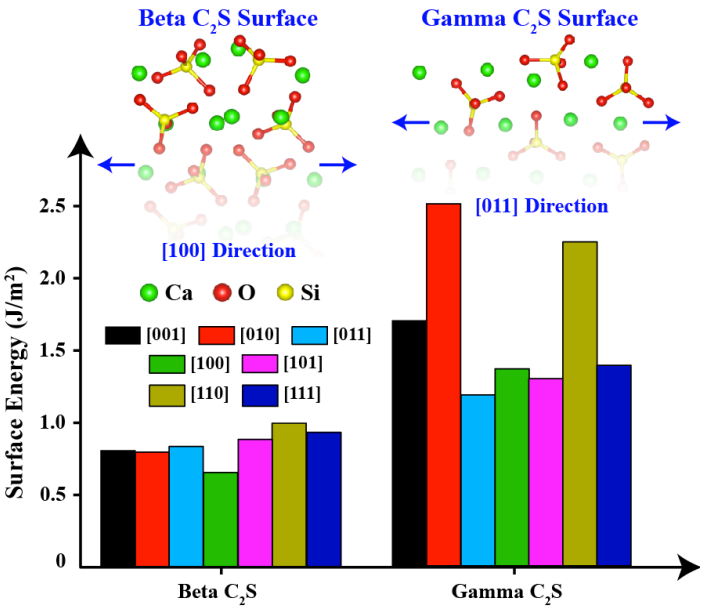
Concrete Sustainability Hub@MIT Research Profile Letter – January 2013

Properties of Polymorphs of Belite

Problem

Portland cement clinker contains four major phases, with alite (C_3S) the most dominant (50-70% by mass) and highly reactive with water, and belite (C_2S) constituting 15-30% of normal cement clinkers and reacting slowly with water. The production temperature of C_2S is lower than that of C_3S making a long-standing challenge the improvement of the reactivity of C_2S phase in order to increase its use, which could result in lower energy requirements. Engineering belite requires a deep fundamental understanding of the physical and chemical properties of different polymorphs of belite. At ordinary pressures, thermal and X-ray measurements have reported five different polymorphs, including Beta (β), Gamma (γ), and three Alpha (α) phases. In all normal portland cement clinkers, C_2S contains stabilizing ions to prevent transformation from β- to γ-C_2S. Even though β and various α phases have similar atomic arrangements, the γ polymorph is different and has a lower density. Exploring the chemical, physical, and mechanical properties of the lower temperature polymorphs, β and γ, are the subject of this investigation.



Energetics of Beta and Gamma C_2S surfaces. The least energetic surface structures are indicated.

Approach

First-principles fully quantum mechanical analytical techniques are applied to the modeling of different polymorphs of belite. Combined with statistical analyses, we predict the energetically most favorable structures of β and γ polymorphs. We calculate the substitution and formation energies for most of the dominant impurities (Al, K, Fe, Mg) and vacancy defects. We examine how each impurity (dopant, vacancy, *etc.*) defect affects the reactivity of the material. By calculating the surface energies for all *adatoms* (atoms adsorbed into the crystal structure) in all polymorphs, we aim to understand how adatoms and defects play a role in determining surface energies and crystal reactivity.

Findings

The γ-C_2S polymorph forms after cooling β-C_2S below 500°C. Calculated cohesive energy of γ-C_2S is the highest, establishing the stability of this polymorph. Charge density of γ-C_2S in the lowest unoccupied molecular orbitals is lower than that of β-C_2S which signals lower reactivity. Our initial calculations demonstrate that adatoms influence the reactivity of γ-C_2S more than that of β-C_2S. Surface energies shown in the figure for γ-C_2S polymorphs are higher than those of β-C_2S. However after the addition of impurities in our simulations, calculated surface energies of γ-C_2S polymorphs decreased significantly.

Impact

This research provides new information about polymorphs of belite obtained by atomic scale modeling. Results of impurity defects, which vary reactivity for γ-C_2S and β-C_2S polymorph, can be used to control reactivity of belite. Information on surface energetics of polymorphs with impurities can shed also light on grinding processes.

More

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