



Ideal strength, phonon stability and thermodynamics of the CrB-type CaX^{IV} ($\text{X}^{\text{IV}} = \text{Si, Ge, and Sn}$) binary compounds



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ABSTRACT

We reported a theoretical investigation of the ideal strengths, dynamical and thermodynamic properties of the CrB-type CaX^{IV} ($\text{X}^{\text{IV}} = \text{Si, Ge, and Sn}$) alkaline-earth metal compounds by employing density functional theory (DFT) and density functional perturbation theory (DFPT). The calculated ideal tensile strengths have the sequence of $\text{CaSi} > \text{CaGe} > \text{CaSn}$ for these intermetallic compounds along the [100], [010], and [001] high-symmetry lines. The present results mean the tensile and shear abilities of CaSi are best, followed by CaGe and CaSn calcium-based compounds. Based on the linear response method within DFPT, the full phonon dispersion curves and the phonon densities of state of the CaX^{IV} ($\text{X}^{\text{IV}} = \text{Si, Ge, and Sn}$) intermetallic compounds are investigated systematically. Furthermore, the Raman-active and Infrared-active phonon modes at Γ point of Brillouin Zone (BZ) center are assigned combining with the point group theory. Our calculated results indicate that three calcium-based compounds are all dynamically stable at ambient conditions. Additionally, within the calculated vibration phonon densities of states, the thermo-physical properties of three calcium-based compounds such as the vibration internal energy, Helmholtz free energy, the lattice entropy and the lattice heat capacity have been also obtained. These investigations serve for new references for further synthesis of various calcium-based alkaline-earth metal compounds.

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1. Introduction

The Ca- X^{IV} ($\text{X}^{\text{IV}} = \text{Si, Ge, and Sn}$) binary systems present many peculiar physical and chemical properties, they have received more and more research interests from the multitudinous scientists due to their extensive applications in solar cells, thermoelectronic converters and other emerging industrial fields [1–9]. These alkaline-earth metal compounds have been well characterized, and the investigations on their basic physical and chemistry properties may capture more useful information. Owing to the scientific and technological interest of Ca- X^{IV} ($\text{X}^{\text{IV}} = \text{Si, Ge, and Sn}$) intermetallics, the studies on the various fundamental properties are becoming very imperative in the current.

Manfrinetti's research group [2–4] investigated the phase diagram of the Ca-Si, Ca-Ge, and Ca-Sn systems across almost the wide composition range in terms of differential thermal analysis, metallographic analysis, X-ray diffraction and even electron microscopy techniques. They confirmed a series of intermediate

phases [2–4]: i.e., CaSi_2 (CaSi₂-type), $\text{Ca}_{14}\text{Si}_{19}$ (Ca₁₄Si₁₉-type), Ca_3Si_4 (Ca₃Si₄-type), CaSi (CrB-type), Ca_5Si_3 (Cr₅B₃-type), Ca_2Si (anti-PbCl₂-type), CaSn_3 (AuCu₃-type), CaSn (CrB-type), $\text{Ca}_{31}\text{Sn}_{20}$ (Pu₃₁Rh₂₀-type), Ca_2Sn (Co₂Si-type), Ca_7Sn_6 (Ca₇Sn₆-type), $\text{Ca}_{36}\text{Sn}_{23}$ (Yb₃₆Sn₂₃-type), Ca_5Sn_3 (Cr₅B₃-type), Ca_2Ge (anti PbCl₂-type), Ca_5Ge_3 (Cr₅B₃-type), CaGe (CrB-type) and CaGe_2 (CaSi₂-type). Among these intermetallic compounds, the equiatomic composition CaX^{IV} ($\text{X}^{\text{IV}} = \text{Si, Ge, and Sn}$) systems present the CrB-type microscope structure, they melt congruently at 1320 °C, 1210 °C, and 1010 °C, respectively [2–4]. Boudierba et al. [10,11] investigated Ca-Ge intermetallics by first-principles calculations within DFT method, they studied the structural parameters, enthalpies of formation, as well as temperature and pressure effects on the phase stabilities of Ca-Ge systems. Yang et al. [12] calculated the structural, elastic, and electronic properties of twenty Ca-X (X = Si, Ge, Sn, and Pb) intermetallic compounds, the results show that CaX^{IV} ($\text{X}^{\text{IV}} = \text{Si, Ge, and Sn}$) compounds are mechanically stable, and the bulk moduli decrease with the increasing of X^{IV} atomic weights. So far, some research groups have systematically carried out the thermodynamic assessment of Ca-Si, Ca-Ge, and Ca-Sn systems by using different approaches [13–15].

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To the best of our knowledge, the theoretical predictions of the CrB-type CaX^{IV} ($\text{X}^{\text{IV}} = \text{Si, Ge, and Sn}$) at ambient conditions are still lacking, in particular, so far the ideal strengths and lattice dynamical properties of CaX^{IV} ($\text{X}^{\text{IV}} = \text{Si, Ge, and Sn}$) remain uncertain. The ideal strengths could evaluate accurately the mechanical performance of a solid, while the dynamical stability is one of the essential conditions which can evaluate the crystal's stability. The scarce of systematical information about the mechanical and dynamical properties of these calcium-based compounds hinders the accurate understandings and the extensive applications. Therefore, with such a purpose, we make an attempt to explore the tensile and shear properties, phonon dispersion relations and thermo-physical properties of three CrB-type CaX^{IV} ($\text{X}^{\text{IV}} = \text{Si, Ge, and Sn}$) compounds with orthorhombic structure (*oC8-Cmcm*) from first-principles method within the high-precision projector augmented wave (PAW) framework [16].

This paper is arranged as follows: section 2 deals with a systematical description of DFT and DFPT approaches that we use to investigate the mechanical, dynamical, and thermo-physical properties for CaX^{IV} ($\text{X}^{\text{IV}} = \text{Si, Ge, and Sn}$). Section 3 is purely devoted to our simulation results and analysis as well as the comparison with the available experiments and other theoretical results. Finally, section 4 summarizes the innovations of *ab initio* study.

2. Methodology

All calculations are performed by first-principles approach under the frames of DFT and DFPT implemented in the Vienna *ab initio* simulation package (VASP) code [17–20]. We have employed the high-precision frozen-core projector augmented wave (PAW) technique of Bloechl [16] to mimic the Coulomb interactions between core ions and valence electrons. The exchange–correlation terms were treated using the generalized gradient approximation (GGA) within the Perdew–Burke–Ernzerhof (PBE) type [21]. The kinetic-energy cutoff for the plane-wave basis was taken to be 500eV determined by repeated convergence tests. A $15 \times 15 \times 15$ grid used for integration in the irreducible Brillouin Zone (BZ) of the reciprocal space was found to be sufficient to obtain the total energy of self-consistent convergence 10^{-7} eV/cell, and the maximum force converged to lower than 0.01 eV/Å.

In order to determine the ideal strengths of three calcium-based compounds, the stress–strain responses have been calculated by incrementally stretching the CaX^{IV} ($\text{X}^{\text{IV}} = \text{Si, Ge, and Sn}$) simulation cells along three specified strain uniaxial directions. In the present calculations, we employ the Nielsen–Martin scheme to gain the corresponding stress for the respective strain by applying the formula as follows [22],

$$\sigma = \frac{(1 + \varepsilon)}{V(\varepsilon)} \frac{\partial E(\varepsilon)}{\partial \varepsilon} \quad (1)$$

$$\tau = \frac{1}{V(\gamma)} \frac{\partial E(\gamma)}{\partial \gamma} \quad (2)$$

where ε is the tensile strain, and γ is the shear strain. $E(\varepsilon)$ and $E(\gamma)$ are the strain energies, $V(\varepsilon)$ and $V(\gamma)$ are the cell volumes at the given tensile and shear strains, respectively.

The phonon spectra and the corresponding density of phonon states (PDOS) calculations are performed using the linear response method within density functional perturbation theory (DFPT) method [23,24] as implemented in VASP code and Phonopy code [25]. We have built a $2 \times 2 \times 2$ supercell consisting of 64 atoms to obtain the force constant matrices and the phonon frequencies.

Also, the vibration contributions to the thermodynamic functions are estimated by the calculated PDOS in the framework of the quasi-harmonic approximation (QHA) [26]. For all investigations, the convergence tests demonstrate that all the parameters used in the calculation produce excellent converged effect, and consequently they are sufficiently large to remove the effects of errors due to Pauli stress in the course of the cell relaxation.

3. Calculated results and analysis

3.1. The crystal structures and electronic densities of state

The binary CaX^{IV} ($\text{X}^{\text{IV}} = \text{Si, Ge, and Sn}$) compounds with CrB-type crystallize the orthorhombic structure (space group: *oC8-Cmcm*) [27]. Fig. 1 displays their crystal structures. For a primitive cell, two Ca atoms and two X^{IV} ($\text{X}^{\text{IV}} = \text{Si, Ge, and Sn}$) atoms are inclusive, both Ca atoms and X^{IV} ($\text{X}^{\text{IV}} = \text{Si, Ge, and Sn}$) atoms are at the Wyckoff position 4c (0, y, 0.25). In the present study, the crystal structures of CaX^{IV} ($\text{X}^{\text{IV}} = \text{Si, Ge, and Sn}$) compounds have been optimized fully to calculate the physical properties. We relaxed all structural degrees of freedom including the volume, ion position, as well as cell shape thoroughly. The optimized equilibrium lattice constants of three CrB-type CaX^{IV} ($\text{X}^{\text{IV}} = \text{Si, Ge, and Sn}$) compounds have been tabulated in Table 1, which compare very well with the available experimental data [28,29] with the errors less than 0.87%, and the results are also in good agreement with Yang et al.'s ultrasoft pseudopotentials calculations values [12]. As can be seen from Table 1, the increasing of molecular weight from CaSi to CaSn produces increasing crystal structure parameters *a*, *b*, and *c*. In this paper, the following other *ab initio* calculations are performed based on the present optimized equilibrium lattice constants.

We also calculated the formation enthalpies and cohesive energies of CaX^{IV} ($\text{X}^{\text{IV}} = \text{Si, Ge, and Sn}$) compounds. The calculated formation enthalpies and cohesive energy of CaX^{IV} ($\text{X}^{\text{IV}} = \text{Si, Ge, and Sn}$) compounds, along with available experimental values and theoretical results [10,12–15,30,31] are tabulated in Table 2. It is shown that the calculated formation enthalpies are in good agreement with the available theoretical and experimental results [10,12–15,30,31]. The calculated results suggest that the CrB-type CaX^{IV} ($\text{X}^{\text{IV}} = \text{Si, Ge, and Sn}$) compounds are thermodynamic stability systems.

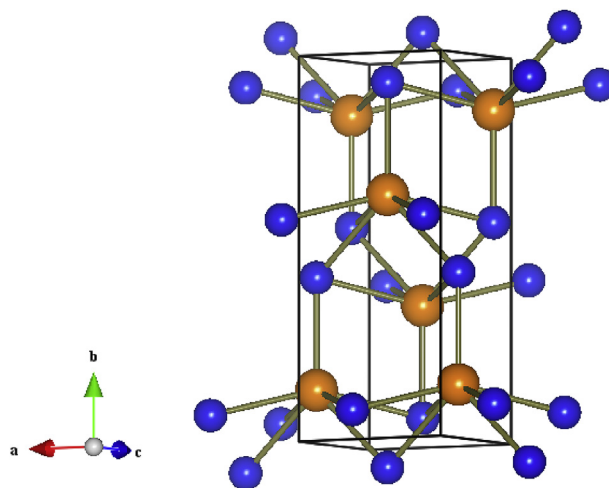


Fig. 1. Crystal structure of CaX^{IV} ($\text{X}^{\text{IV}} = \text{Si, Ge, and Sn}$) with CrB-type (The yellow spheres represent Ca atoms, and the blue spheres represent Si, Ge, or Sn atoms). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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