Predicted CsSi Compound: A Promising Material for Photovoltaic Applications

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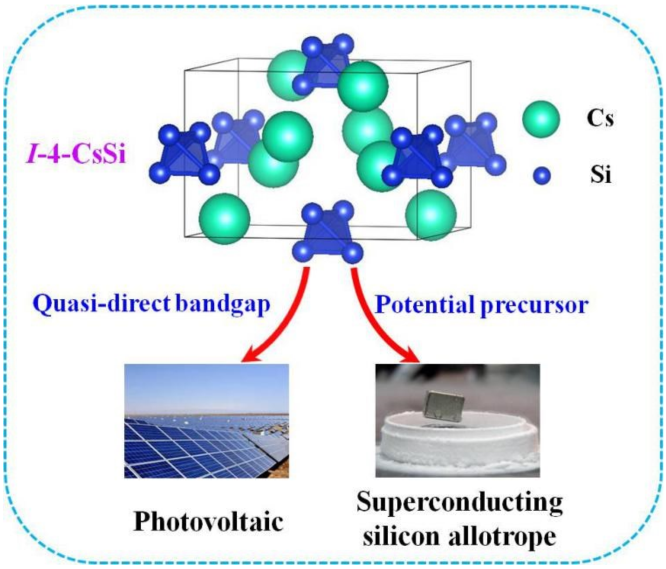
Abstract

Exploration of photovoltaics materials has received enormous interest in a wide range of both fundamental and applied research. Therefore, in this work, we identify a CsSi compound with a Zintl phase for a promising candidate of photovoltaic materials by using global structure prediction method. Electronic structure calculations indicate that this phase possesses a quasi-direct band gap of 1.45 eV, suggesting that its optical properties could be superior to diamond-Si for capturing sunlight from the visible to the ultraviolet range. In addition, a novel silicon allotrope is obtained by removing Cs atoms from this CsSi compound. The superconducting critical temperature of this phase was estimated as a T_c of 9 K in terms of a substantial density of states at the Fermi level. Our findings represent a new promising CsSi material for photovoltaic applications, as well as a potential precursor of a superconducting silicon allotrope.



Caption: The structure of *I*-4-CsSi, a potential photovoltatic material and precursor of a superconducting silicon allotrope.

Introduction

The search for a candidate material for solar energy has attracted great attention, since it is a promising and available renewable resource for its abundant, clean, and sustainable merits.[1-5] Photovoltaics (PV), as important one for solar energy, could directly convert sunlight into electricity, where silicon-based materials are commonly accepted to be the most common PV materials.[6,7] Compared to non-silicon-based PV materials, such as GaAs, CdS, $CuInSe_2$, silicon-based materials have their own advantages, including stability, nontoxicity and low cost. However, due to silicon's indirect fundamental band gap (1.1 eV) and much wider direct band gap (3.4 eV)[8], it is still far from the optimal value (around 1.4 eV) for solar cell applications.[9] Silicon can react with other elements to form a variety of stable binary Zintl phases, which were named after the pioneering chemist Eduard Zintl.[10] Zintl phases are intermetallic compounds that contain a strongly electropositive metal, such as an alkali metal, alkaline earth metal, or lanthanoid, and a somewhat less electropositive metal (typically from the late d block or the early p block).[11-14] In Zintl silicides, electron charge could transfer to the silicon atoms from other elements, forming a variety of sub-network structures with Si–Si covalent bonds.[14-16] In past decades, Zintl silicides have drawn much attention owing to their excellent physical and chemical properties.[17-32]

Among Cs-Si Zintl silicides, CsSi, $Cs_{8-x}Si_{46}$ and Cs_7Si_{136} have been studied in experimentally. The ambient pressure phase of CsSi is thought to adopt the KGe structure type (space group *P*-43*n*, Z=32),[33,34] while the high-pressure phase adopts the NaPb structure type (space group *I*41/*acd*, Z=32).[35] Meanwhile, it is found that the Clathrate-I phase of $Cs_{8-x}Si_{46}$ and Clathrate-II phase of Cs_7Si_{136} can be obtained using CsSi as a starting material via under high pressure or thermal decomposition.[36,37] Recently, a semiconducting *Im*-3*m* symmetry $CsSi_6$ phase is predicted.[38] Moreover, alkali metal silicides are found to be important precursors in the preparation of new silicon allotropes, which can be synthesized by oxidation or thermal decomposition to remove the metal atoms.[39] For example, a new *Cmcm*-Si_6 phase with a quasi-direct band gap near 1.3eV was obtained by removing Na from Na_4Si_{24}.[40] Furthermore, an *Im*-3*m* symmetry Si allotrope with a band gap of 1.17eV is predicted to be stable after removing Cs from *Im*-3*m* $CsSi_6$,[38] and also, a metallic *P*6/*m*-Si_6 allotrope with an interesting T_c of 12.2K at ambient pressure was proposed via a *P*6/*m*-$NaSi_6$ compound as a precursor.[41]

As mentioned above, it is still required to search for new PV materials for science interests and potential application. In this work, we predict a new CsSi compound with a Zintl phase at ambient pressure. Electronic structure calculations reveal that it is a semiconductor with a quasi-direct band gap of 1.45 eV. Moreover, the optical properties of this phase exceeded those of diamond-Si (*dia*-Si) as indicated from the simulations. CsSi, based on our simulations, could be a precursor material to synthesize a *Immm* symmetry silicon allotrope by removing the Cs atoms. *Immm*-Si_4 is dynamically and thermally stable, and also exhibits remarkable superconductivity feature at atmospheric pressure.

Computational details

CsSi compounds are predicted at ambient pressure via the CALYPSO (Crystal structure Analysis by Particle Swarm Optimization) methodology,[42,43] combined with first-principles calculations. This method has been successfully used for the prediction of new stable and mestastable materials.[44-47] The *ab initio* structural relaxations and electronic properties calculations were performed within the framework of density functional theory (DFT) as implemented in the Vienna *Ab-initio* simulation package (VASP).[48] The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE)[49] functional was used to approximate the electronic exchange and correlation interaction. We used projector augmented wave (PAW)[50] potentials with $5s^2 5p^6 6s^1$ and $3s^2 3p^2$ electrons treated as valence for Cs and Si atoms, respectively. An energy cutoff of 700 eV and dense Monkhorst–Pack k-meshes were used to ensure the total energies were converged to within around 1 meV/atom in the structural optimizations. Phonon calculations were performed to determine the dynamical stability of the predicted structures using a supercell approach as implemented in the PHONOPY package.[51] Since the semi-local DFT PBE functional is known to underestimate the band gap of predicted structures, the hybrid Heyd-Scuseria-Ernzerhof functional (HSE06)[52] was used to calculate the electronic and optical properties. The electron phonon coupling constant was obtained from first-principles density-functional perturbation theory as implemented in the QUANTUM ESPRESSO package.[53] Ultrasoft pseudopotentials and an energy cutoff of 80 Ry were employed, with a 3 × 5 × 5 *q*-grid and 12 × 20 × 20 *k*-grids. The broadening for which was converged to within 0.001 was 0.04Ry.

Results and discussion

Herein, the computational prediction of novel CsSi structures was carried out using the particle swarm method with simulation cells of up to four formula units at ambient pressure. Our structure search identified a previously unknown orthorhombic CsSi Zintl phase (space group *I*-4, 16 atoms/cell), as shown in Fig. 1. In our predicted *I*-4-CsSi structure, silicon atoms form isolated tetrahedra, corresponding to the typical characteristics of Zintl monosilicides with an alkali metal. At ambient pressure, the optimized lattice parameters are a = 10.107Å and c = 7.022Å, with Cs atoms occupying the 8*g* (0.112, 0.259, 0.909) and Si atoms occupying the 8*g* (0.115, 0.96, 0.619)Wyckoff sites. A Bader charge analysis[54] revealed that 0.68*e* are transferred from the Cs atoms to the Si atoms in *I*-4-CsSi.

The phase stability of *I*-4-CsSi was investigated by calculating the enthalpy of formation, which is given via $\Delta H = [H(\mathrm{CsSi}) - H(\mathrm{Cs}) - H(\mathrm{Si})]/2$, where *H*(CsSi) is the enthalpy of *I*-4-CsSi, *H*(Cs) is the enthalpy of elemental bcc Cs, and *H*(Si) is the enthalpy of elemental Si in the diamond structure. The formation enthalpies of the known *P*-43*n* and *I*41/*acd*-CsSi phases were also considered in our simulations. The enthalpy of *I*41/*acd*-CsSi is lower than that of the *P*-3*n* structure above 3.3 GPa, indicating that the *I*41/*acd* phase becomes stable above this pressure, which is consistent with the experimental preparation of *I*41/*acd*-CsSi at 4 GPa.[35] Our results revealed that ΔH of *I*-4-CsSi is -0.032 eV/ atom at ambient pressure, which is 27 and 50 meV/atom higher than that of *I*41/*acd* and *P*-43*n*-CsSi, respectively. To investigate the dynamic stability of *I*-4-CsSi, we computed the phonon dispersion curves at ambient pressure, as shown in Fig.2a. There is no imaginary frequency in the whole Brillouin Zone, demonstrating the dynamically stable nature of our predicted *I*-4-CsSi. The *I*-4-CsSi compound is thus a low-lying metastable phase. With increasing the pressure to 49.2 GPa, *I*-4-CsSi becomes enthalpically more favorable than *P*-43*n*-CsSi, although *I*41/*acd* still remains the most stable phase.

For materials used in PV devices, the band gap is a critical parameter because the conversion efficiency from sunlight into electrical power is a function of the band gap. The electronic band structure of *I*-4-CsSi was calculated, as shown in Fig. 2b. It is well known that the PBE functional normally underestimates the band gap, while the screened hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE) usually gives more accurate electronic band gaps. *I*-4-CsSi was calculated to have a band gap of 1.42 eV with the HSE06 functional, and 0.92 eV with the PBE functional, from the minimum of the conduction band at the M-point to the maximum of the valence band close to the Γ-point along the Γ-Z direction. The direct band gap of *I*-4-CsSi, which is located at the M-point, was 1.45 eV with the HSE06 functional (0.93 eV with PBE), indicating that *I*-4-CsSi is a semiconductor with a quasi-direct band gap.

To further explore the potential applications for photovoltaic devices, we simulated the optical absorption spectrum of *I*-4-CsSi using the HSE06 functional, as shown in Fig. 3. The calculated absorption spectrum of the *dia*-Si phase is also simulated for comparison with the reference air mass (AM) 1.5 solar spectral irradiance.[55] For *I*-4-CsSi, the absorption of low-energy photons starts from ~1.5 eV, which is close to its band gap. The *I*-4-CsSi phase exhibits considerably stronger absorption than *dia*-Si in the visible light range of 1.7-3.2eV, and the absorption spectrum overlaps significantly with the solar spectrum. The decrease of the direct optical band gap as compared to that of *dia*-Si is beneficial for improving the absorption, thus, the photo current of the solar cell. This suggests that the *I*-4-CsSi phase could potentially be employed in highly efficient Si-based solar cells.

It is well known that Zintl phases play a critical role as precursors for the synthesis of Si and Ge allotropes or other metastable compounds using chemical oxidation and thermal decomposition. Thus, the Cs atoms in the *I*-4-CsSi structure were removed to obtain the pure silicon allotrope. After fully structural optimization, the phase evolved into a new orthorhombic silicon allotrope with the *Immm* space group (Fig. 4a). This *Immm*-Si_4 phase contains open channels formed from six-membered Si rings along the crystallographic *c* axis, and differs markedly from the tetrahedral motifs present in the *I*-4-CsSi structure.

The silicon sublattice of the product differs from that of the precursor has been found experimentally in the formation of Ge allotropes by oxidation of $Na_{12}Ge_{17}$ or Na_4Ge_9.[56,57] The Na atoms template the formation of the Ge_{136} framework as the $[Ge_4]^{4-}$ and $[Ge_9]^4$- polyanions are oxidized and are then emptied from the clathrate framework cages as the reaction progresses.[39] The transformation of polyanionic clusters into the Ge_{136} framework requires not only new Ge-Ge bonds to be formed but also existing Ge–Ge bonds to be broken. [39] At ambient pressure, the optimized lattice parameters of *Immm*-Si_4 are a = 6.195, b = 3.248, and c = 3.496 Å, with Si atoms occupying the 4*e* (0.191, 0.5, 0.5) Wyckoff sites. The bond lengths of Si_1-Si_2 and Si_1-Si_3 are 2.495 and 2.368 Å, respectively (Fig. 4a).

The total energies of the experimentally known *dia*-Si, R8,[58,59] *Cmcm*-Si_6,[40] and *Fd*-3*m*-Si_{136}[60] phases, and the theoretically predicted *Immm*-Si_4, and *P*6/*m*-Si_6[41] phases of silicon were calculated. Fig.4b shows that *dia*-Si is the most thermodynamically stable phase, as expected. The total energies of *Cmcm*-Si_6 and *P*6/*m*-Si_6 are 0.09eV/atom and 0.35eV/atom higher than that of *dia*-Si, respectively, which is in good agreement with previous computations.[41] Moreover, the energy of *Immm*-Si_4 is lower than that of *Fd*-3*m*-Si_{136}, a phase that has been synthesized using thermal decomposition.[60] Fig. 4c shows no imaginary frequencies are observed in *Immm*-Si_4 throughout the whole Brillouin zone, indicating that it is dynamically stable at ambient pressure.

To further understand the electronic properties, we calculated the band structure and density of states of *Immm*-Si_4, as shown in Fig. 4d. The results indicate that *Immm*-Si_4 exhibits metallic behavior. The previously reported pure Si allotropes are almost semiconductors except the recently proposed metallic *P*6-*m* Si phase with T_c of 12.2 K at ambient pressure.[41] Therefore, we calculated the electron-phonon coupling constant, λ, from first-principles density-functional perturbation theory, and the superconducting critical temperature, T_c, was estimated using the Allen-Dynes-modified McMillan formula,[61,62] with a Coulomb pseudopotential μ^* of 0.1. The logarithmic average of phonon frequencies, $\omega_{\log}$, and λ obtained from the Eliashberg spectral function, $\alpha^2F(\omega)$, were 259 K and 0.70, respectively. Our results predict that the *Immm*-Si_4 allotrope is a superconducting phase with an estimated T_c of 9 K at ambient pressure.

Conclusions

In summary, we predicted an *I*-4-CsSi compound via crystal structure search carried out at ambient pressure. Compared to the known CsSi phases, it is thermally metastable and dynamically stable. Electronic structure calculations indicate that *I*-4-CsSi has a quasi-direct band gap of 1.45 eV, which perfectly matches the optimal value of ~1.4 eV for solar cell applications. The calculated optical absorption of *I*-4-CsSi reveals that its optical properties are superior to those of *dia*-Si. Moreover, a novel silicon allotrope of *Immm*-Si_4 was obtained by removing Cs atoms from the *I*-4-CsSi compound followed by structural relaxation. *Immm*-Si_4 is dynamically stable at ambient pressure with an estimated T_c value of 9 K. *Immm*-Si_4 is 0.05eV/atom more stable than the previously synthesized *Fd*-3*m*-Si_{136} phase, indicating that it is likely to be synthesized in the lab. Our current results represent that *I*-4-CsSi is not only a new promising material for photovoltaic applications, but also a potential precursor of a novel superconducting *Immm*-Si_4 allotrope.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

The acknowledgements come at the end of an article after the conclusions and before the notes and references. This research was supported by the Natural Science Foundation of China (11504007 and 11704151), and the Scientific and Technological Research Project of the‘13th Five-Year Plan’ of Jilin Provincial Education Department (JJKH20200031KJ and 201649). The work was also supported by the Foster Program of Youth Research Innovation Team and Program of Young Teacher Promotion in Beihua University. E. Z. acknowledges the NSF (DMR-1827815) for financial support.

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Figure Caption

Fig. 1 Predicted CsSi structure. (a) A polyhedral view. (b) A view along the c axis.

Fig. 2 Calculated (a) phonon dispersion, and (b) band structure of *I*-4-CsSi using the PBE (black lines) and HSE06 (red lines) functionals.

Fig. 3 The optical absorption spectrum of *I*-4-CsSi and dia-Si.

Fig. 4 (a) The crystal structure of *Immm*-Si_4. (b) Energy vs volume curves of various silicon allotropes. (c) Phonon dispersion, Eliashberg spectral function, and electron phonon coupling integral, as well as (d) The band structure and total densities of states of the *Immm*-Si_4 phase at ambient pressure.

Fig.1

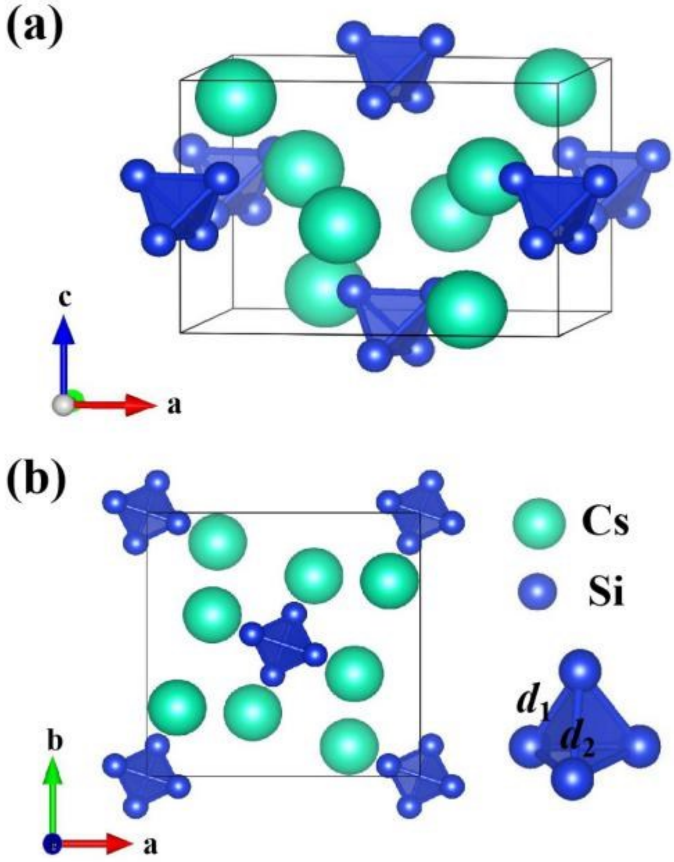

Fig.2

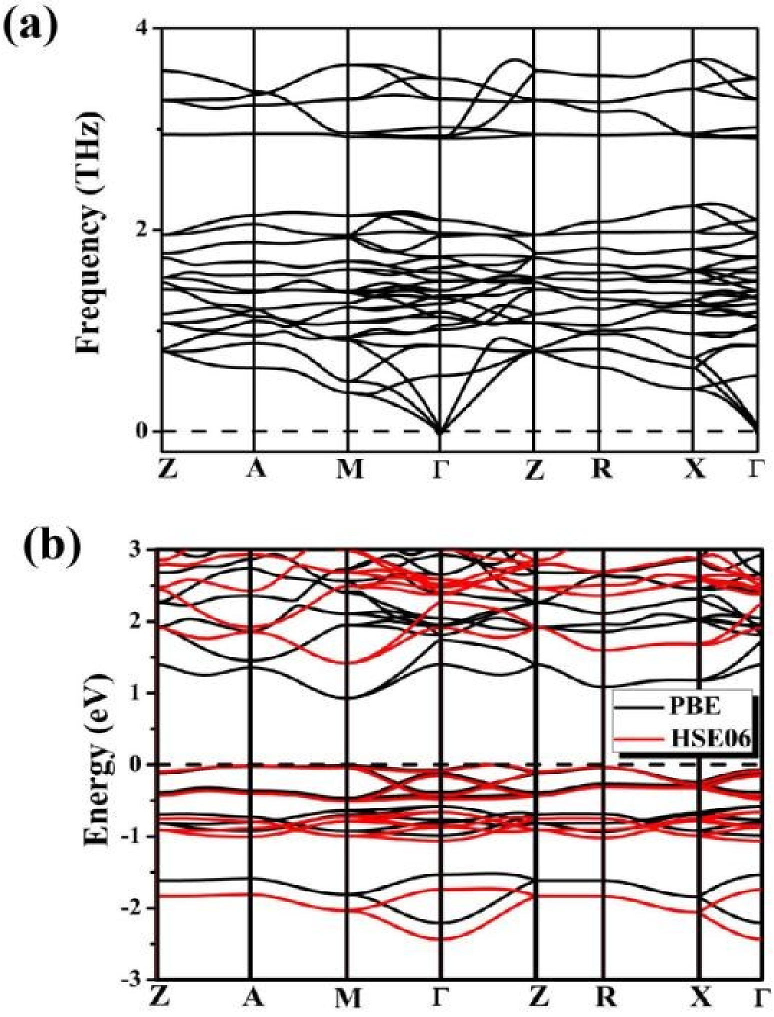
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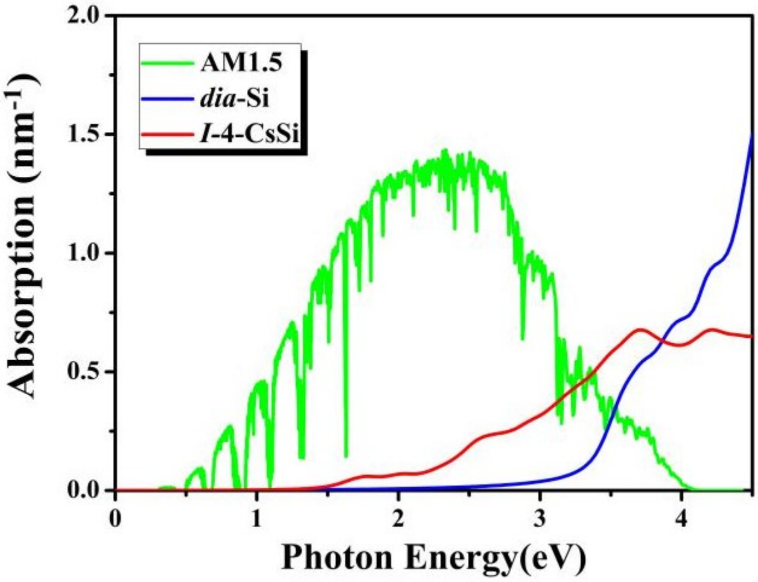
Fig.3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I-4-CsSi
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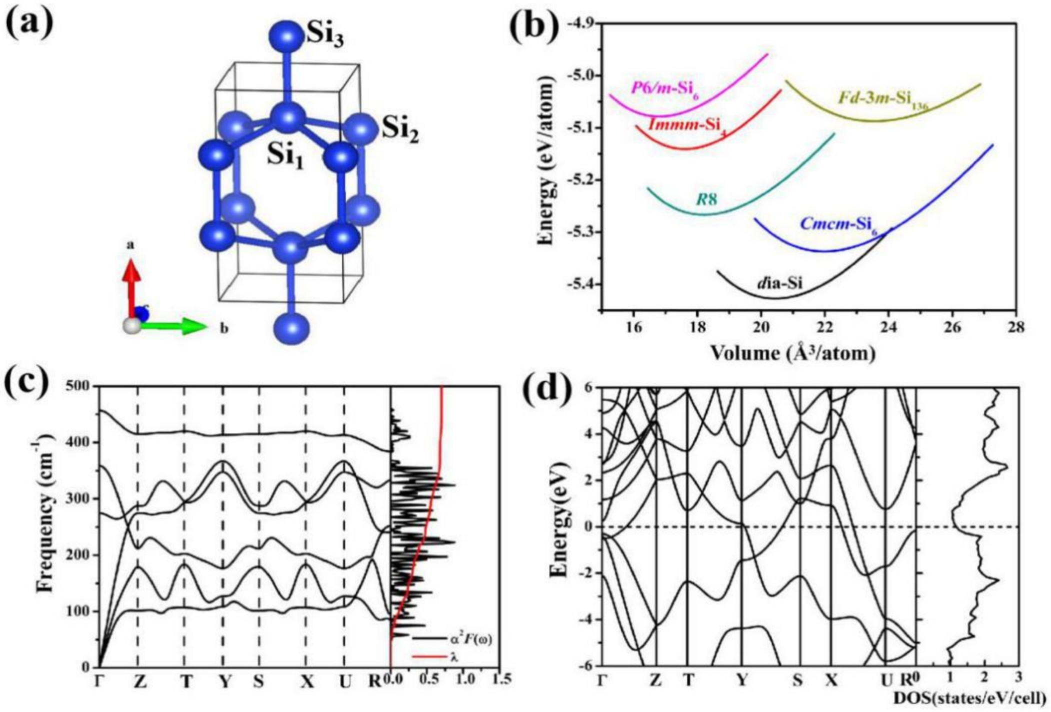
Fig.4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Energy (eV/atom)
Volume (Å3/atom)
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Fd-3m-Si136
R8
Cmcm-Si6
dia-Si
-4.9
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-5.1
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-5.3
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16
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Frequency (cm-1)
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1.0
1.5
α2F(ω)
λ
(d)
Energy(eV)
6
4
2
0
-2
-4
-6
Γ
Z
T
Y
S
X
U
R
0
1
2
3
DOS(states/eV/cell)