

# Electronic Structure and Optical Properties of C-Doped Ca<sub>2</sub>Si

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**Abstract.** A first-principle method is used to calculate the geometric structure, energy band structure, electronic state density, and optical properties of C-doped Ca<sub>2</sub>Si. Results show that volume of Ca<sub>2</sub>Si decreases, and band gap increases after doping with C. The optical properties of Ca<sub>2</sub>Si after C doping change as follows:  $\epsilon_1(\omega)$  and refractivity index increase, whereas  $\epsilon_2(\omega)$ , extinction coefficient, absorption, and reflectivity decrease.

## 1. Introduction

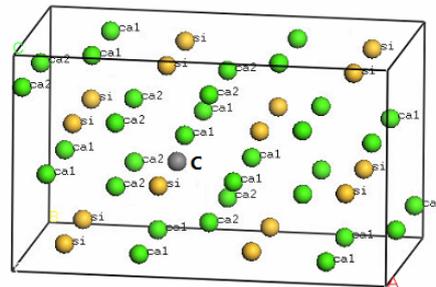
Ca<sub>2</sub>Si is a direct band gap semiconductor. This material is a potential and ideal semiconductor material given its higher light absorption coefficient than that of  $\beta$ -FeSi<sub>2</sub> [1]; Ca<sub>2</sub>Si also demonstrates good compatibility with existing silicon-based technology and thus is expected to be used as a high-performance solar cell, which has been widely studied. Studies on Ca<sub>2</sub>Si started in 1989 in Italy when Bisi et al. identified that Ca<sub>2</sub>Si is a semi-metal by using the muffin-tin orbital method, and experimental results on light emission and reflective emission demonstrated that Ca<sub>2</sub>Si is a semiconductor [2]. Since then, the number of reports on Ca<sub>2</sub>Si has increased. For instance, Takagi et al. used evaporative heat treatment, a two-step method, to prepare single-phase Ca<sub>2</sub>Si crystals for the first time [3–4]. Matsui [5] prepared a first single-phase Ca<sub>2</sub>Si thin film by using the displacement method involving Mg<sub>2</sub>Si. Yang Yin Ye et al. [6] used magnetron sputtering technology to obtain single-phase Ca<sub>2</sub>Si film directly migrating on a Si (100) substrate. Doping is an effective approach to modulate the characteristics of semiconductors. Theoretical reports on doped Ca<sub>2</sub>Si remain few. By using a first-principle method, Xiao Qingquan et al. [7] determined the electronic structure of Ca<sub>2</sub>Si. Feng Yun et al. [8–9] calculated the effects of K doping on the electronic structure and optical properties of Ca<sub>2</sub>Si. Ran Yaozong et al. [10] studied the electronic structure and optical properties of Sc-doped Ca<sub>2</sub>Si. Cen Weifu et al. [11–12] determined the effects of P doping and the (111), (001), (110), and (100) plane strains on the band structure and optical properties of Ca<sub>2</sub>Si. These studies showed that n-type semiconductors form in the orthorhombic structure after Sc and P doping, whereas p-type semiconductors form in the orthorhombic and cubic phases after K doping. First-principle investigation on doping Ca<sub>2</sub>Si remains limited to K, P, and Sc doping, and no studies have been conducted on doping and optical properties of C-doped Ca<sub>2</sub>Si. C and Si belong to the same family and possess the same valence. Few studies on doping of the same element have been reported. Duan Xingkai et al. [13] have used experimental methods to study the incorporation of Sn at different concentrations. With changes in Sn concentration, electrical conductivity and thermal conductivity of Ca<sub>2</sub>Si significantly improved. Theoretical studies on doping of elements belonging to the same group



in  $\text{Ca}_2\text{Si}$  have not been reported. Therefore, in this study, the first-principle method is used to determine the electronic structure and optical properties of C-doped orthorhombic  $\text{Ca}_2\text{Si}$ , providing a theoretical basis for the modification of doping in  $\text{Ca}_2\text{Si}$ .

## 2. Models and methods

The orthorhombic  $\text{Ca}_2\text{Si}$  cluster space is Pnma (No. 62) with the following lattice constants:  $a = 0.7667$  nm,  $b = 0.4779$  nm and  $c = 0.9002$  nm [1]; each cell consists of eight Ca atoms and four Si atoms. In this study, the supercell of a  $\text{Ca}_2\text{Si}$  crystal consists of 48 atoms, each of which expands to a single cell in the direction of  $a$ , with  $b$  serving as basis of  $\text{Ca}_2\text{Si}$  cells to obtain a  $2 \times 2 \times 1$  superlattice. C-doped  $\text{Ca}_2\text{Si}$  is calculated with one C atom instead of Si atom. Figure 1 shows the calculation model involving C instead of Si.



**Figure 1.** Calculation model

All calculations are performed using the CASTEP software package [14]. First, the lattice constant is optimized by the Broyden–Fletcher–Goldfarb–Shanno algorithm. The exchange correlation potential adopts the method of generalized gradient approximation. Ultra-soft pseudopotentials used to deal with the interaction between ions and electrons. In calculation of total energy and charge density, the plane-wave cutoff energy measures 310 eV, and the Brillouin zone integration is a  $3 \times 3 \times 3$  Monkhor–Pack form high-symmetric special k-point method. The valence electron configurations selected in the calculation include  $4s^2$  of Ca,  $3s^23p^2$  of Si, and  $2s^22p^2$  of C.

## 3. Results and analysis

### 3.1 Geometric structure

Table 1 shows the physical parameters obtained after optimization. The lowest energy of  $\text{Ca}_2\text{Si}$  doped with one C measures  $-33333.6100$  eV, which is 455.2025 eV higher than that of undoped  $\text{Ca}_2\text{Si}$ . After doping, the lattice constant  $a$  slightly increases, whereas  $b$  and  $c$  decrease. Thus, the corresponding volume also decreases. This result is obtained as the atomic radius of C atoms is smaller than that of Si. C doping can distort the lattice of  $\text{Ca}_2\text{Si}$  and alter the position of atoms in the unit cell, thereby affecting the electronic structure and optical properties of  $\text{Ca}_2\text{Si}$ .

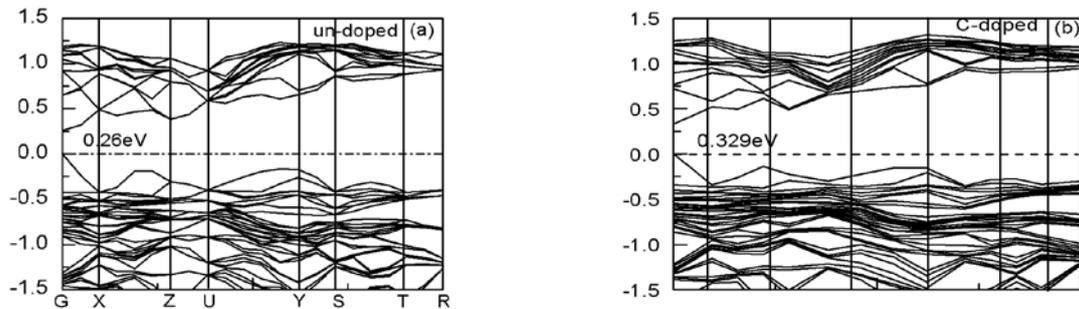
**Table 1.** Lattice constants of  $\text{Ca}_2\text{Si}$  and C-doped  $\text{Ca}_2\text{Si}$

| Sample   | $2a/\text{nm}$ | $2b/\text{nm}$ | $c/\text{nm}$ | $v/\text{nm}^3$ | Total energy/eV |
|--|----------------|----------------|---------------|-----------------|-----------------|
| Un doped $\text{Ca}_2\text{Si}$ (experimental) | 1.5334         | 0.9598         | 0.9002        | 1.3248          | -----           |
| Un doped $\text{Ca}_2\text{Si}$ (Calculated)   | 1.5221         | 0.9705         | 0.9080        | 1.3412          | $-33788.8125$   |
| C-doped $\text{Ca}_2\text{Si}$                 | 1.5228         | 0.9672         | 0.8990        | 1.3240          | $-33333.6100$   |

### 3.2 Band structure and density of states

Figure 2 shows the energy band structure before and after C doping.  $\text{Ca}_2\text{Si}$  is a direct bandgap semiconductor as shown in Figure 2(a). The G band corresponds to the top of the band and to the bottom of the conduction band. Bandgap width reaches 0.26 eV, which is slightly smaller than the

0.36 eV reported by Imai et al.; this result is attributed to the structural optimization and convergence that allow different conditions to lead to deviations in K point, resulting in slight deviation in the band gap [12]. After C doping,  $\text{Ca}_2\text{Si}$  remains as a direct band gap semiconductor, but its energy band structure changes. The bandgap corresponding to G point reaches 0.329 eV, the conduction band becomes dense and translates upward, the valence band becomes dense, and the band structure near the Fermi surface becomes complex.

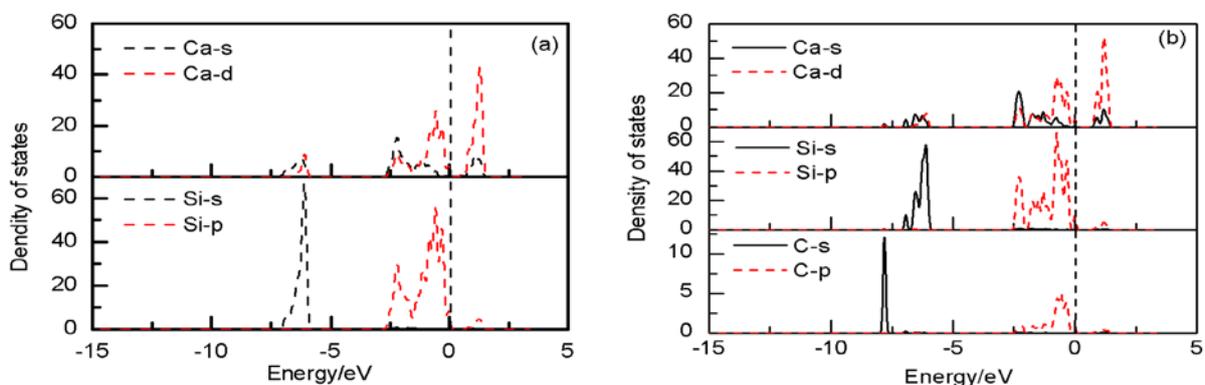


**Figure 2.** Band structure of  $\text{Ca}_2\text{Si}$  near the gap (a) and (b) C-doped  $\text{Ca}_2\text{Si}$

Figure 3 shows the density before and after C doping. As shown in Figure 3 (a), the bottom of the conduction band of undoped  $\text{Ca}_2\text{Si}$  mainly contributes to Ca 3d, whereas the contribution of Ca 4s is relatively minimal. The top valence band is mainly contributed by Si 3p and Ca 3d, and the contribution of Ca 4s is relatively small. After C doping, the bottom conduction band contributes to Ca 3d 4s, whereas the top valence band contributes to Si 3p, Ca 3d, and C 2p. The peak value of the 3d states of the conduction band of Ca and the density of the 3p states of the partial valence band of the valence band have increased. Although C and Si feature the same valence states, their electronegativity values differ. The electronegativities of C and Si total 2.55 and 1.90, respectively. After C replaces Si, the valence electrons in Ca are attracted more easily, and the radii of C and Si atoms measure 0.91 and 1.46 Å, respectively. Electron binding capacity than Si.

### 3.3 Optical properties

In the linear range, the optical properties of semiconductors can be described by the complex dielectric function  $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ . The imaginary part  $\epsilon_2(\omega)$  of the dielectric function can be calculated by the momentum transition matrix element between the occupied and non-occupied states. According to the Kramers–Kronig relationship and the definition of direct transition probability, the real part  $\epsilon_1(\omega)$ , absorption coefficient, refractive index, extinction coefficient, and reflection coefficient can all be deduced, although they will not be described here in detail.



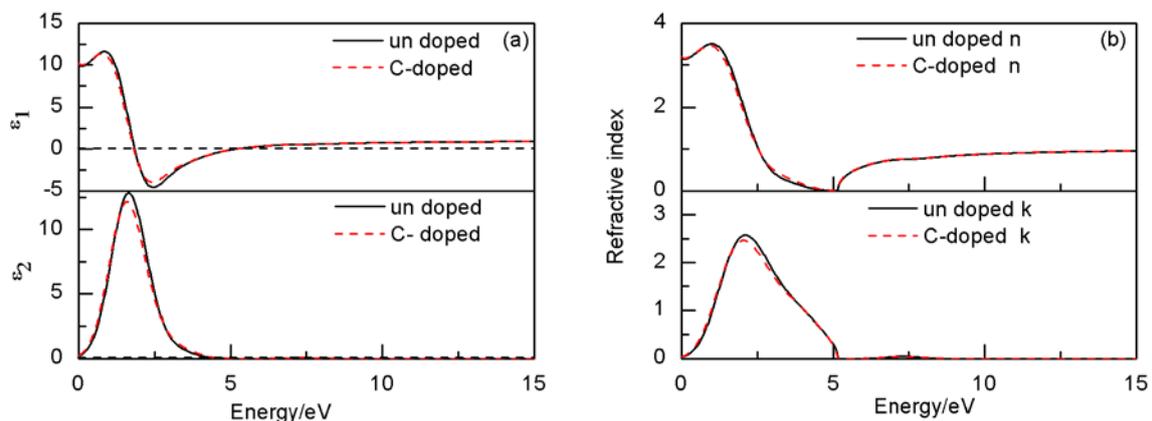
**Figure 3.** State density of un-doped  $\text{Ca}_2\text{Si}$  (a) and (b) C-doped  $\text{Ca}_2\text{Si}$

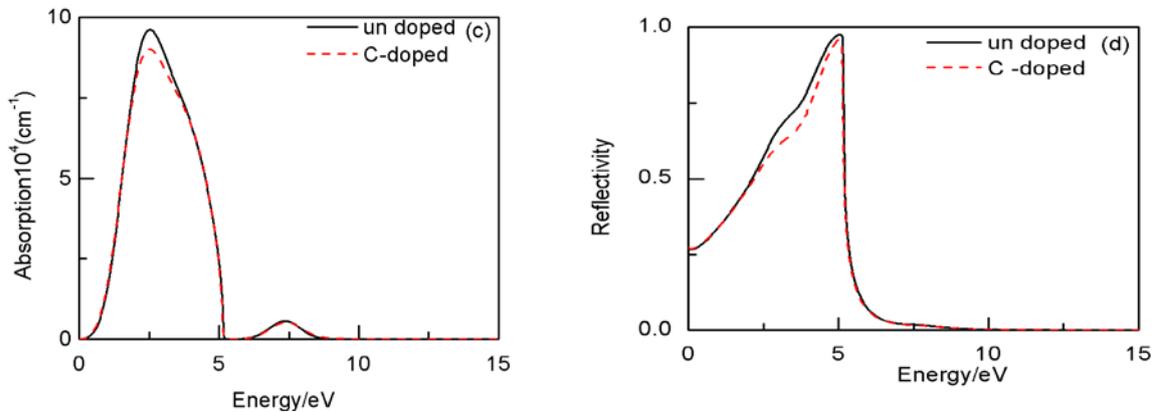
Figure 4(a) shows the real and imaginary parts of  $\text{Ca}_2\text{Si}$  with energy before and after C doping. The figure shows that the trend for C doping is consistent with that for undoped  $\text{Ca}_2\text{Si}$ . The static dielectric constant  $\epsilon(0)$  of  $\text{Ca}_2\text{Si}$  = 10.04 eV and  $\epsilon(0)$  = 10.21 eV after C doping, and the static dielectric function increases, corresponding to the changes in the refractive index in Figure 4 (b). The imaginary part of the dielectric function is important for any material and reflects the solid band structure and various spectral information. The undoped  $\text{Ca}_2\text{Si}$  in Figure 4 (a) shows that the dielectric peak of  $\epsilon_2(\omega)$  is 12.826 at 1.64 eV. As shown in the density of states in Figure 3, the peak at 1.64 eV results from the optical transition between Si 3p and Ca 3d. After C doping,  $\epsilon_2(\omega)$  shows a dielectric peak at 1.60 eV, but the first dielectric peak decreases to 12.165. Thus, after C doping, the imaginary part of the dielectric peak moves slightly toward the low-energy direction and the peak value decreases. This phenomenon is attributed to the larger binding energy of the C atom to the outer electron than that of Si, and C 2d is less likely to undergo optical transition compared with Si 3d.

Figure 4 (b) shows the birefringence of  $\text{Ca}_2\text{Si}$  before and after C doping. The main peak of  $n$  appears at 0–1.5 eV, the maximum peak appears at 1.01 eV, and the peak value is 3.5042. After reaching the maximum peak, the refractive index decreases with increasing energy. After C doping,  $n_0$  = 3.197 and the dielectric peak still appears at 0–1.5 eV. As shown in Figure 4 (b), the maximum extinction coefficient of  $\text{Ca}_2\text{Si}$  totals 2.574 at 2.118 eV, and then  $K$  decreases as energy increases. At 10.10 eV, the extinction coefficient is zero. After C doping, the trend for extinction coefficient is consistent with that for before doping, wherein the peak decreases and moves slightly toward the low-energy side, corresponding to the change in dielectric function in Figure 4 (a).

Figure 4 (c) shows the absorption coefficient of  $\text{Ca}_2\text{Si}$  before and after C doping. The undoped  $\text{Ca}_2\text{Si}$  exhibits two major peaks, which are found at positions 2.52 and 7.36. After C doping, two absorption peaks are observed, and the main absorption peak is observed at 2.50 eV. The peak decreases significantly. The absorption peak mainly originates from the valence band electron conduction band transition of the excited state, and the decrease in absorption peak indicates that the transition process reduces due to C incorporation. The absorption peak at 7.39 eV is attributed to the optical transition from the 3S state electron of Si to the conduction band bottom.

Figure 4 (d) shows the reflection spectra of  $\text{Ca}_2\text{Si}$  before and after C doping. The band transition in undoped reflection band mainly occurs within 4.45–5.12 eV, and the average reflectivity can reach up to 90%. After C doping, transition ranges of the reflection bands and reflectivity decrease, indicating that the reflectivity of  $\text{Ca}_2\text{Si}$  decreases after C doping.





**Figure 4.** Optical properties of undoped and C-doped Ca<sub>2</sub>Si; (a) dielectric function; (b) refractive index; (c) absorption; and (d) reflectivity.

#### 4. Conclusion

The geometry, energy band structure, density of states, and optical properties of C-doped Ca<sub>2</sub>Si are calculated using the density functional theory-based first-principle calculations. After C doping, the lattice constant *a* of Ca<sub>2</sub>Si slightly increases, whereas *b* and *c* and the lattice volume decrease. The undoped band gap of 0.26 eV increases to 0.329 eV, the bandgap broadens, and the contribution of Ca 3d and Si 3p near the Fermi surface increases. In terms of optical properties, the binding energy of C atoms to outer electrons is higher than that of Si. C 2d is less likely to demonstrate optical transition compared with Si 3d. After doping, static permittivity and refractive index increase; the imaginary part of the dielectric peak moves slightly to the lower-energy direction, the peak value decreases, and the extinction coefficient, absorption coefficient, and reflectivity decrease. These results show that although C doping affects the optical properties of Ca<sub>2</sub>Si, its effect is considerably small.

#### 5. Acknowledgements

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