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# The Effect on the Electric Structure and Optical Properties of $Ca_2Ge$ Bulk with Sr-Doping

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## Abstract

The electronic structure and the optical properties of $Ca_2Ge$ have been calculated by the first-principles pseudo potential method. The results of the electric structure show that $Ca_2Ge$ bulk is a direct semiconductor with the band gap of 0.306 eV, the conduction band is mainly composed of Ca 3d, the valence band is mainly composed of Ge 3p. With Sr-doping, $Ca_2Ge$ bulk is a direct semiconductor with the band gap of 0.350 eV, the conduction bands are mainly composed of Ca 3d and Sr 3d, the valence bands are mainly composed of Ge 3p and Sr 3d. The results of the optical properties show that the dielectric constant of $Ca_2Ge$ bulk is reduced from 21.52 to 13.94, the reflectivity is decreased, and the absorption is increased with Sr-doping. The optical properties are improved with Sr-doping, the results offer theoretical guide for the optical properties control of $Ca_2Ge$.

## Keywords

$Ca_2Ge$, Electronic Structure, Optical Properties, First Principle, Sr-Doped

## 1. Introduction

The alkaline-earth metal of $Ca_2Ge$ is a new environmental friendly semiconductor material, the existence of multiple germander phases in the Ca-Ge system leads to the simultaneous formation of $Ca_2Ge$, $Ca_5Ge_3$, CaGe, $Ca_3Ge_4$, $CaGe_2$, $Ca_7Ge_6$ and so on during growth process. However, $Ca_2Ge$ is a direct semiconductor, has a simple orthorhombic structure and a cubic structure (The orthorhombic structure, which is a stable phase with an energy band gap of is 0.26 eV) [1] [2] [3] [4] [5]. $Ca_2Ge$ has attracted much attention for its potential to create new classes of environmentally conscious elec-

tronics [6]. Recently, the study of $Ca_2Ge$ has a definite progress while is started relativity late, so the related literature reports and data available for reference. In 2003, the abinito method was used to study the geometric construction of $Ca_2Ge$ by D. B. Migas, the results showed that $Ca_2Ge$ was demonstrated had an orthorhombic and a cubic crystal system [3]. In 2010, Yang used the first-principles method based on the density functional theory to study the electric structure of $Ca_2Ge$, the results showed that $Ca_2Ge$ was a direct band gap semiconductor material with the band gap of 0.265 eV [4]. In 2015, Jun used the first-principles method base on the density functional theory to study the photon correlation spectroscopy of $Ca_2Ge$, the results showed that the photon frequency of $Ca_2Ge$ was lower than $Ca_2Si$ in the low energy region; the results provide reference for the photoelectric properties of $Ca_2Ge$ in the next phase study [6]. The dielectric function is described the polarization response of the material under the condition of the electric field, it as a bridge establish the connection between microscopic photon excitation, electronic transmission associate and macroscopic visible optical properties, revealing the macroscopic dielectric properties of the micro mechanism. While, in order to improve the optical properties of $Ca_2Ge$, using the first principles pseudo-potential method to study the electric structure of $Ca_2Ge$ with Sr-doping, discuss the influence of dielectric function of $Ca_2Ge$ with Sr-doping, and study the regulated mechanics of the optical properties of $Ca_2Ge$.

## 2. Calculation Method

The simple orthogonal $Ca_2Ge$ bulk belongs to the space group of Pnma (No.62), the lattice constant are a = 7.804 Å, b = 4.896 Å, c = 9.204 Å. Each primitive cell contains 8 Ca atoms and 4 Ge atoms [7]. **Figure 1** shows that the position of Ca atom has been the replace by one Sr atom in the internal coordinate of (0.522, 0.250, 0.676). All the possible structures are optimized by the BFGS algorithm (proposed by Broyden, Fletcher, Goldfarb and Shannon) [8] [9] [10] [11], which provides a fast way of finding the lowest energy structure and supports cell optimization in the CASTEP code [12] [13] [14]. The optimization is performed until the forces on the atoms are less than 0.01 eV/Å, and all the stress components are less than 0.02 GPa, the tolerance in the self-consistent field (SCF) calculation is $1.0 \times 10^{-6}$ eV/atom. Ultra-soft pseudo-potentials (USPP) is expanded within a plane wave basis set with 330eV, the iteration convergence accuracy is $1.0 \times 10^{-6}$ eV. The energy of $Ca_2Ge$ have been calculated based on the optimization of structural system, the minimum energy made to be chosen stable structure, the electronic structure and polarization of the dielectric function were calculation. The ionic and electronic interaction was calculated, the Ca 3p 4s, Ge 3p 4s electron made to be chosen valence electron, the k-point sampling are $4 \times 5 \times 3$ according to the Monkhorst-Pack method in the Brillouin Zone (BZ) [15].

## 3. Calculation Results and Discussion

### 3.1. The Crystal Structure

The lattice constants and volume of $Ca_2Ge$ bulk for derails see **Table 1**. The **Table 1**

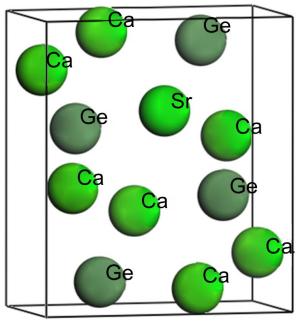



**Figure 1.** The atomic structure of $Ca_2Ge$.

**Table 1.** Geometric structure of $Ca_2Ge$ and doping after optimization.

| Sample | a/nm | b/nm | c/nm | V/nm$^3$ |
|---|---|---|---|---|
| Orth$Ca_2Ge$ | 7.804 | 4.896 | 9.204 | 351.670 |
| Orth$Ca_2Ge$ with Sr-doping | 7.912 | 4.931 | 9.228 | 360.022 |

shows that the lattice constants a, b, c and the original cell volume V are slightly changed with Sr-doping. Comparing with the results of $Ca_2Ge$ bulk it shows that the lattice constant and volume of $Ca_2Ge$ were increased, slightly. The reason is that the atom radius of Sr is larger than Ge and the bond length of Sr-Ge is longer than the Ca-Ge (the atomic radius of Sr is 2.45 Å, the atomic radius of Ge is 1.52 Å).

## 3.2. The Electronic Structure

### 3.2.1. The Energy Band Structure

The energy band structure of $Ca_2Ge$ bulk for derails see **Figure 2**. The **Figure 2(a)** shows that the $Ca_2Ge$ bulk is a direct semiconductor with the band gap of 0.306 eV at the Γ-point. The **Figure 2(b)** shows that the top of valence band and the bottom of the conduction are moved to the direction of the high energy with Sr-doped and is formed a direct semiconductor with the band gap of 0.350 eV at the Z-point. The change is that the configuration of extra-nuclear electron of Ca is $3p^64s^2$, the configuration of extra nuclear electron of Sr is $4p^65s^2$, and the lose electron of Sr is easy than Ca. the results show that $Ca_2Ge$ is a direct band gap semiconductor material with the band gap of 0.35 eV, with Sr-doping.

### 3.2.2. The Density of States

The density of states of $Ca_2Ge$ bulk for derails see **Figure 3**. The **Figure 3(a)** shows that the valence bands are mainly composed of Ge 4p, Ca 3d, the contribution of Ge 3s and Ca 3p are less. The conduction bands are mainly composed of Ca 3d, the contribution of Ge 3p 3s and Ca 3p are less. The **Figure 3(b)** shows that the valence bands are mainly composed of Ge 4p, Ca 3d, Sr 4d, the contribution of Ge 3s and Ca 3p are less. The conduction bands are mainly composed of Ca 3d, Sr 4d, and the contribution of Ge 3p 3s and Ca 3p are less. The effect of density of states of $Ca_2Ge$ bulk with Sr-doped is that the Ge 3p active state is increased in the valence bands and the Ca 3d active state is in-

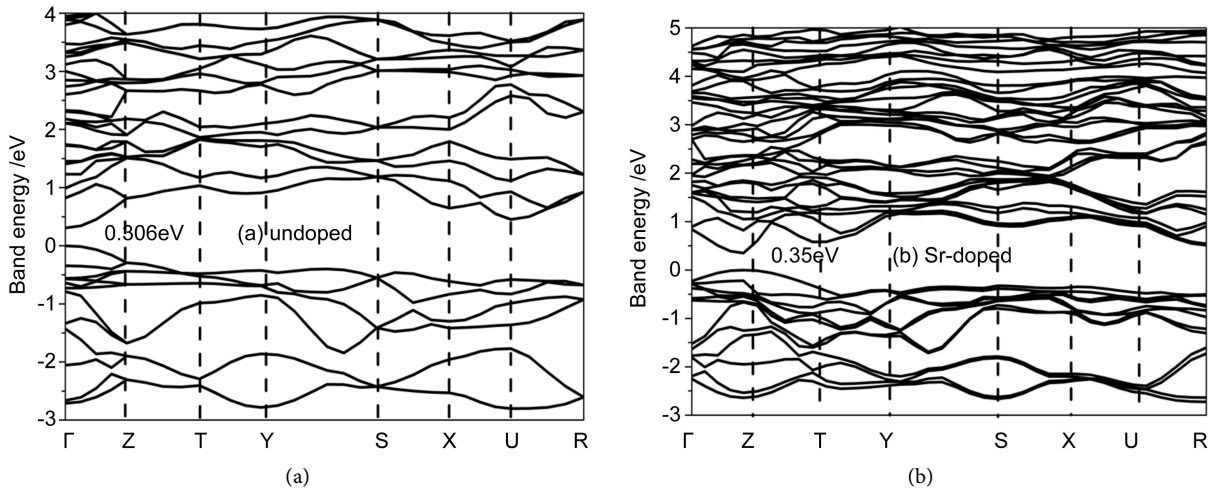



**Figure 2.** The band structure of $Ca_2Ge$. (a) $Ca_2Ge$; (b) Sr-doped $Ca_2Ge$.

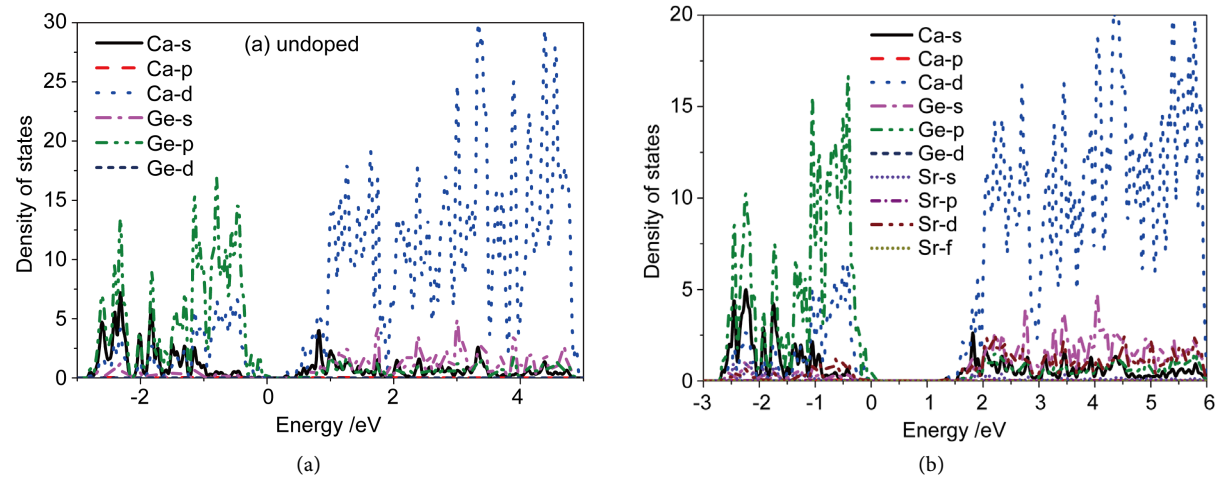


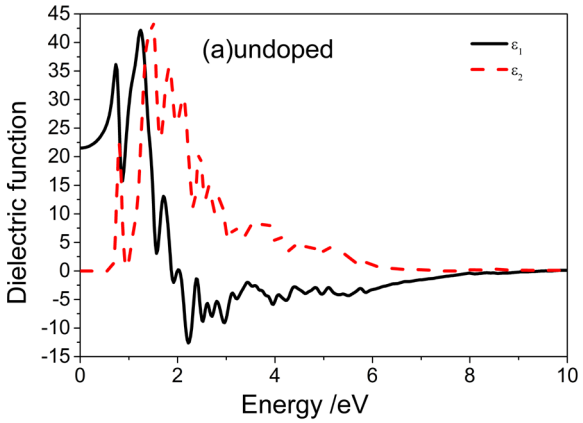

**Figure 3.** Density of states. (a) $Ca_2Ge$; (b) Sr-doped $Ca_2Ge$.

creased in the conduction bands. The valance bands of Sr-doped $Ca_2Ge$ are mainly composed of Ge 4p, Ca 3d and Sr 4d. The conduction bands are mainly composed of Ca 3d, Sr 4d.

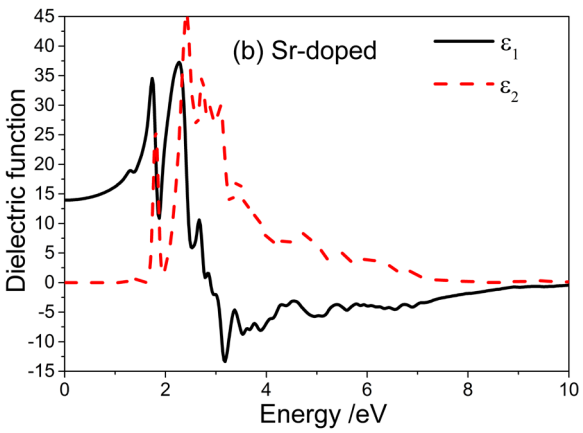
## 3.3. The Optical Properties

### 3.3.1. The Complex Dielectric Function

Figure 4 is the dielectric function of $Ca_2Ge$ bulk. Figure 4(a) shows that the dielectric constant of $Ca_2Ge$ bulk is 21.5 and the dielectric function department is formed two dielectric peaks with the photoelectron energy increasing. The maximum dielectric peak is appeared at 1.3 eV, and the maximum dielectric peak is 42.5. The dielectric function imaginary part is forthcoming when the photoelectron energy is higher than 0.8 eV is formed four dielectric peaks with the photoelectron energy increasing, and it reflected the transition of the electron. Figure 4(b) shows that the dielectric constant $Ca_2Ge$ bulk with Sr-doping is 13.9, and the dielectric function department is formed two




(a)




(b)

**Figure 4.** The dielectric function. (a) $Ca_2Ge$; (b) Sr-doped $Ca_2Ge$.

dielectric peaks with the photoelectron energy increasing. The maximum dielectric peak is appeared at 2.1 eV, and the maximum dielectric peak is 38.5. The dielectric function imaginary part is forthcoming when the photoelectron energy is higher than 1.8eV is formed two dielectric peaks with the photoelectron energy increasing. The effect of the dielectric function of $Ca_2Ge$ bulk with Sr-doped is that the dielectric constant and the maximum dielectric peak are decreased, and it due to the configuration of extra-nuclear electron of Sr is active than Ca. The results show that the dielectric constant of $Ca_2Ge$ bulk is 21.5. The results show that the dielectric constant $Ca_2Ge$ bulk with Sr-doping is 13.9.

### 3.3.2. The Absorption Spectrum

**Figure 5** is the dielectric function of $Ca_2Ge$ bulk. **Figure 5** shows that the absorption edge of $Ca_2Ge$ bulk is appeared at the photoelectron energy of 0.8 eV, and in the energy range of 1.8 - 7.3 eV the absorption spectrum more than 10,000. The absorption edge of $Ca_2Ge$ bulk with Sr-doping is appeared at the photoelectron energy of 1.8 eV, and in the energy range of 2.3 - 10.2 eV the absorption spectrum more than 10,000. The absorption range of $Ca_2Ge$ bulk is increased and the absorption edge is moved to high energy

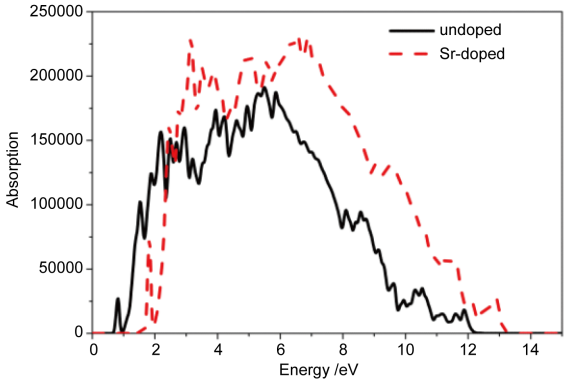



**Figure 5.** The absorption of $Ca_2Ge$.

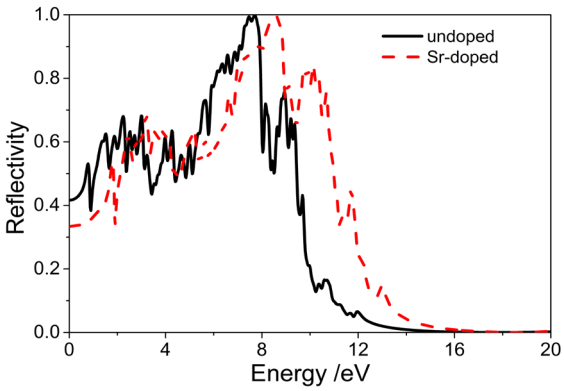



**Figure 6.** Reflectivity spectrum of $Ca_2Ge$.

direction with Sr-doping. The results show that the absorption coefficient decreased.

### 3.3.3. The Reflectivity Spectrum

**Figure 6** is the dielectric function of $Ca_2Ge$ bulk. **Figure 6** shows that the reflectivity of $Ca_2Ge$ bulk is exceed 80% is appeared at the photoelectron energy range of 6.3 - 8.2 eV. The reflectivity of $Ca_2Ge$ bulk with Sr-doping is exceed 80% is appeared at the photoelectron energy range of 7.6 - 8.7 eV. Comparing the reflectivity spectrum found that the reflectivity is moved to the high direction and is decreased the high reflection area with Sr-doping. The results show that the reflection spectrum decreased.

## 4. Conclusion

The electronic structure and optical properties of orthorhombic $Ca_2Ge$ bulk are calculated by first-principles pseudo potential method based on density functional theory. The results show that the forbidden bandwidth is increased, and the optical properties are enhanced with Sr-doping.

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