Computational Materials Science 150 (2018) 346–352

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

DFT + U study on the electronic structures and optical properties of pyrite and marcasite

Yuqiong Li[a], Jianhua Chen[a,b,*], Ye Chen[a], Cuihua Zhao[a,*], Ming-Hsien Lee[c], Tse-Hsing Lin[c]

[a] School of Resources, Environment and Materials, Guangxi University, Nanning 530004, PR China
[b] Innovation Center for Metal Resources Utilization and Environment Protection, Guangxi University, Nanning 530004, PR China
[c] Department of Physics, Tamkang University, New Taipei 25137, Taiwan

ARTICLE INFO

Keywords:
Pyrite
Marcasite
Electronic structures
Optical properties
Density functional method

ABSTRACT

Pyrite is an attractive material as its good photovoltaic performance; however, the presence of marcasite phase is considered to be detrimental to pyrite as a photovoltaic material due to its low band gap. Density functional theory (DFT) combined with Hubbard U correction was used to perform the calculations on the crystal structures, electronic structures, and optical properties of pyrite and marcasite in the present work. When a U value of 1.5 eV is adopted to Fe 3d, the band gaps of pyrite and marcasite are calculated to be 1.05 eV and 1.33 eV, respectively, compared to 0.54 eV and 1.05 eV without adopting U. It is found that the fundamental band gap in pyrite is formed by Fe 3d-S 3p transition while in marcasite it is formed by Fe 3d-Fe 3d transition. The larger band gap of marcasite suggests that the presence of marcasite could not deteriorate the photovoltaic performance of pyrite. The subsequent calculations on the optical properties confirmed a very similar optical absorption performance of marcasite to pyrite, even finding a redshift of the optical absorption edge of marcasite compared to pyrite in the low energy region and a wider absorption range in the high energy region. These results were associated with the Fe octahedron differences in the crystals, which resulted in a different d orbital splitting scheme proposed in our study.

1. Introduction

Pyrite (FeS_2) has gotten much attention due to its high optical absorption coefficient ($> 10^5\,cm^{-1}$) and high quantum efficiency (> 90%) for applications as a photovoltaic material which can be used as ultrathin film. Moreover, it is abundant on the earth and consists of abundant elements with low cost. However, its maximum open-circuit voltage as optical absorber in solar cells was measured only about 0.2 V [1].

The possible reasons of the low open-circuit voltage have been studied. The presence of marcasite phase is considered to be one of the main reasons [2–4]. Marcasite has the same chemical formula as pyrite, but has different spatial structure. These two phases can be transformed to each other under certain conditions, leading to inclusion of marcasite in pyrite. It is thought that the low band gap nature of marcasite decreases the open-circuit voltage of pyrite material. The experimental gap of pyrite is about 0.95 eV [1]; however, the marcasite was rarely reported before. Marcasite was firstly reported behaving a band gap of 0.34 eV [5], and later a theoretical calculation value of 0.4 eV [6]. However, researchers have questioned the result in recent years and re-evaluated the value of band gap mainly based on the theoretical methods. Sun et al. reported first-principles calculation results of 0.88, 0.81, 0.88, 2.72, and 1.2 eV using LDA, GGA-PBE, GGA-AM05, HSE06, and Δ-sol, respectively [3]. GGA method used by Seefeld et al. suggested 0.63 eV [7]. Schena et al. gave 0.80 and 1.06 eV by GGA-PBE and G_0W_0 calculations, respectively [8]. The most recent result by Sánchez et al. who gave a value of about 0.83 eV by diffuse reflectance spectroscopy (DRS) [9]. Most of these results suggest a band gap of marcasite of 0.7–1.0 eV which is believed to be at least as large as pyrite, so the presence of marcasite is thought unlikely to undermine the photovoltaic performance of pyrite [3,7].

The electronic structure of marcasite and the effect of the presence of marcasite on the photovoltaic performance of pyrite are recognized and established gradually in recent years, and the optical absorption experiment of pyrite-marcasite mixed-phase films also has been carried out [8]. However, no more detailed comparison and explanation on the results have been published in the literatures, except the study by Schena et al. who have compared the band structure results of pyrite with marcasite using standard DFT and the GW approximation [8]. Hence the detailed information in crystal and electronic structures and

* Corresponding authors at: School of Resources, Environment and Materials, Guangxi University, Nanning 530004, PR China (J. Chen).
E-mail addresses: jhchen@gxu.edu.cn (J. Chen), xiaocui2000110@163.com (C. Zhao).

https://doi.org/10.1016/j.commatsci.2018.04.009
Received 11 January 2018; Received in revised form 3 April 2018; Accepted 6 April 2018

optical properties, especially their interrelationship are still not well known. This work will focus on the comparison of atomic bonding structures, electron structures, and the optical properties of pyrite and marcasite by theoretic calculations using density functional theory (DFT) with Hubbard U correction (DFT + U).

2. Computational details

Based on density functional theory (DFT), the calculations on electronic structures and optical properties were performed using CASTEP code, GGA-PW91 functional [10]. The Hubbard U correction [11,12] was adopted for treatment of Fe 3d with strongly correlated electrons. Only the valence electrons (Fe $3d^6 4s^2$ and S $3s^2 3p^4$) were considered by use of ultrasoft pseudopotentials [13] and a plane wave cut-off energy of 350 eV after testing. Monkhorst-Pack *k*-point sampling density for pyrite was 6 × 6 × 6 mesh and for marcasite 6 × 5 × 7. The self-consistent field (SCF) convergence tolerance was set to 2.0×10^{-6} eV·atom^{-1}. The spin-polarized was chose.

Pyrite (cubic symmetry) with the space group $Pa\bar{3}$ and cell parameter of 5.4160 Å was used in our calculations [14]. For marcasite, the crystal space group *Pnnm* with cell parameters of a = 4.4446 Å, b = 5.4246 Å, c = 3.3864 Å was used [14].

3. Results and discussion

3.1. Structural properties

The unit cells of pyrite and marcasite are shown in Fig. 1. Pyrite contains four Fe and eight S atoms in the cell with formula Fe_4S_8, and marcasite contains two Fe and four S atoms in the cell with formula Fe_2S_4. We compared the results of using and without using Hubbard U correction. The Hubbard U correction [11,12] was adopted for treatment of Fe 3d. The application of U correction will give a more precise band gap value of the material. In our previous study, the U value was tested on pyrite from 0 to 2.5 eV and then 1.5 eV of U was chosen in this work where the band gap of pyrite was calculated to be 1.05 eV [15], very close to the experimental value 0.95 eV [1]. The total energies of pyrite and marcasite are calculated to be −1425.64 eV and −1425.68 eV per FeS_2 unit without the use of Hubbard U correction, respectively, and −1424.48 eV and −1424.52 eV per FeS_2 unit with the use of Hubbard U correction, respectively. This result suggests that the stability of pyrite and marcasite is nearly the same. However, the relative stability of pyrite and marcasite may change with the use of functionals. Seefeld et al. suggested that marcasite was more stable than pyrite using GGA exchange-correlation functional [7], while Sun et al. found that within the LDA and AM05, pyrite is the ground state [3]. The work of Spagnoli et al. using GGA-PBEsol and GGA-AM05 XC functionals predicted pyrite as being more stable than marcasite, while LDA and GGA-PBE predicted an opposite result [2].

Table 1
Lattice parameters of pyrite and marcasite and Mulliken populations of bonds in them. Mulliken bond population, i.e. bond order, higher population suggesting stronger covalency.

		Pyrite	Marcasite
Calculated lattice parameter (Å)	DFT	a = b = c = 5.3799	a = 4.4157, b = 5.3822, c = 3.3768
	DFT + U	a = b = c = 5.3876	a = 4.4073, b = 5.3818, c = 3.3848
Experimental lattice parameter (Å)		a = b = c = 5.4160	a = 4.4446, b = 5.4246, c = 3.3864
DFT + U calculations on bond length (Å)/ Mulliken population	Fe–S	2.251/0.33	2.219/0.27 2.240/0.64
	S–S	2.154/0.27	2.222/0.12

The detailed lattice parameters of pyrite and marcasite and Mulliken populations of bonds in the minerals are shown in Table 1. DFT + U calculations predict a lattice parameter of 5.3876 Å for pyrite, and a = 4.4073 Å, b = 5.3818 Å, and c = 3.3848 Å for marcasite, very close to the experimental values of 5.4160 Å for pyrite, and a = 4.4446 Å, b = 5.4246 Å, and c = 3.3864 Å for marcasite [14], suggesting the reliability of the calculation. These two crystals have the same atomic coordination, i.e. six-coordinated Fe by S atoms, and four-coordinated S by three Fe atoms and one S atom. The pyrite Fe octahedron shares corners, whereas the marcasite Fe octahedron shares edges. The six Fe–S bond lengthens are equal in pyrite but not equal in marcasite, in that pyrite has an equal Fe–S length of 2.251 Å, while marcasite has two different Fe–S bond lengthens of 2.240 Å and 2.219 Å, resulting in less regular Fe octahedron in marcasite.

We calculated the Mulliken bond population (bond order).The larger the bond population is, the greater the covalency of the bond is [16]. Results suggest that the bond population of Fe–S (0.33) is slightly larger than S–S (0.27) in pyrite, while in marcasite they are of great difference. The bond populations of Fe–S1, Fe–S2 and S1–S3 in marcasite are 0.27, 0.64, and 0.12, respectively. Observing from the crystal structure it is indicated that in marcasite the covalent interaction of Fe–S bond along the y-direction is much weaker than that along the x- and z-directions. In addition, it is apparent that the S–S bond length (2.222 Å) in marcasite is much larger than that (2.154 Å) in pyrite, and the bond populations of the former and the latter are 0.12 and 0.27, respectively, suggesting the covalent interaction of the former is much weaker than that of the latter.

We analyzed the bond angles in the two crystals, as shown in Table 2. There are one kind of Fe–S–Fe angle and one kind of Fe–S–S

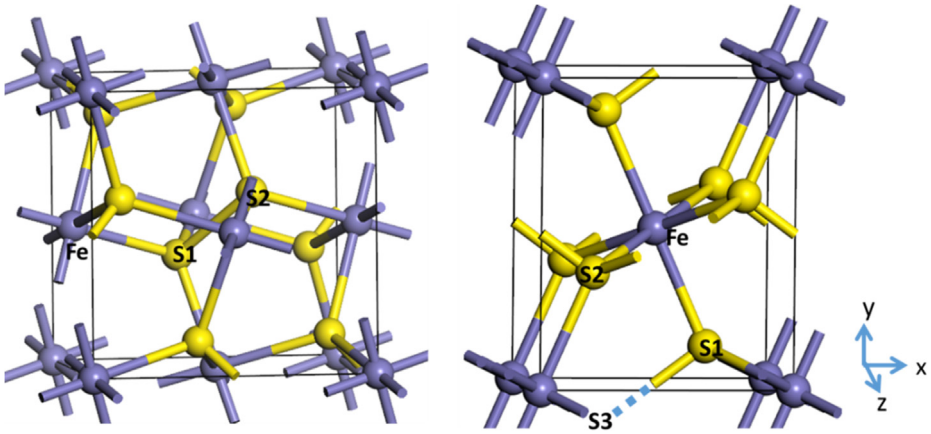

Fig. 1. Unit cells of pyrite (left) and marcasite (right).