High-pressure induced phase transition of FeS₂: electronic, mechanical and thermoelectric properties.

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Abstract

Being as the most abundant natural mineral among the iron-based sulphides, iron pyrite (FeS₂) has been extensively investigated. These investigations mainly focused on the known marcasite (*Pnnm*) and pyrite (*Pa* $\bar{3}$) phases, due to unknown of high pressure (HP) structural phases of FeS₂. Here, we report a theoretical study up to 300 GPa to uncover a brand new monoclinic HP phase of *C2/m* structure at above 192 GPa. The stable of this structure is evaluated by the thermodynamical, dynamical and mechanical calculations. The *C2/m* structure is characterized by distorted FeS₆ octahedron together with two connected 1D zigzag-like *S* chains. Analysis of the thermoelectric calculations indicates that the electronic thermal conductivity and electrical conductivity of *C2/m* structure linearly increasing with increasing temperature. Meanwhile, it is found that the *C2/m* phase behaves in a ductile manner through the elastic parameters calculations.

Keywords: High Pressure , First Principle, Structure Prediction, Thermoelectric Properties.

1. Introduction

The studies of iron-based sulphides have been of considerable interest in the last few decades because of their broad range of optical, magnetic, and electronic properties that made them potentially attractive for various technological applications [1-4]. Among the

iron-based sulphides, iron pyrite (FeS_2) is the most abundant natural mineral, and its polymorphic structure has been extensively investigated both theoretically and experimentally [5-8]. At ambient conditions, FeS_2 crystallizes in an orthorhombic $Pnnm$ structure (marcasite) and acts as a non-magnetic semiconductor [9,10]. Based on the electrical resistivity measurements [11], its energy gap was found to be 0.34 eV. Performing this structure under pressure, it undergoes a first-order phase transition to a cubic $Pa\bar{3}$ structure (pyrite) at around 3.7 GPa [12]. The effects of hydrostatic pressure on the electronic structures of pyrite has been investigated [13], revealing that the semiconductor pyrite is transforming into a metal pyrite at 94 GPa. Apart from several experimental and theoretical studies of the spectroscopic and thermoelectric properties of the FeS_2 [12, 14,15], however, no more research is related to the activity of FeS_2 under HP has been found thus far. Meanwhile, the structural phases and properties of FeS_2 under HP remained unknown.

Here, we report a theoretical study on an investigation of HP structures of FeS_2 at pressure range 50–300 GPa. The theoretical approach involved the use of calypso methodology [16-18] for structure prediction, which is unbiased by any prior known structural information. Our structure prediction revealed a brand new HP structural phase transitions into a monoclinic $C2/m$ structure. The first-principle calculations have confirmed the mechanical, dynamical and thermodynamical stabilities of this phase. Moreover, the electronic properties investigation suggested that $C2/m$ possess good metallic features and its thermoelectric properties showed enhancement of electrical conductivity with increasing temperature.

2. Computational details

We performed global minimization of FeS_2 (at $T = 0$ K) by merging *ab initio* total energy calculations and the calypso technique on structural predictions, as implemented in the CALYPSO code [16-18]. The CALYPSO method has been successful to correctly predict HP structures for various systems [19-23]. The underlying *ab initio* electronic structure calculations and geometry relaxations were performed in the framework of density functional theory (DFT) using the Perdew–Burke–Ernzerhof (PBE)

exchange–correlation functional [24] within GGA as implemented in the *Vienna ab initio simulation package* (VASP) code [25]. The Fe ($3d^7 4s^1$) and S ($3s^2 3p^4$) are treated as valence electrons by adopting the electron projector-augment wave (PAW) method [26] with PAW pseudo-potentials, which has been tested to be more applicable at HP. Energy cutoff of 600 eV has been used within *ab initio* electronic structure calculations and the $4 \times 7 \times 7$ Monkhorst-Pack [27] grid for the k-points sampling are used for the $C2/m$ structure to ensure that all the enthalpy calculations are well converged to less than 1 meV/atom. Phonon dispersions calculations are carried out using the supercell approach as implemented in the PHONOPY code [28]. Thermoelectric properties were performed using Boltzmann transport equation as implemented in BOLTZTRAP code [29]. Elastic constants of optimized crystal structure of $C2/m$ were calculated by the strain-stress method and the elastic modulus were thus derived from the Voigt-Reuss-Hill averaging scheme [30, 31].

3. Result and Discussions

3.1 The structural phase stability of FeS₂

By using CALYPSO-code interfaced with VASP, we have chosen the simulation cells containing 1-4 formula units (f. u.) to predict the structures of FeS₂ at pressure range 50–300 GPa. Several structures are generated through the predictions search and the lowest enthalpy structures were obtained (where the free energy reduces to enthalpy at $T = 0K$). At low pressure, we successfully found the reported *marcasite*-FeS₂ (space group $Pnnm$) and *pyrite*-FeS₂ (space group $Pa\bar{3}$) structures [32], which validating our method adopted here. At HP ranges, a brand new structure of FeS₂ (space group $C2/m$) was successfully found with simulation cells containing four formula units. The lower enthalpy difference curves for the predicted structures as functions of pressure are presented in Figure 1. As shown in Figure 1, the predicted $C2/m$ structure has more favorable enthalpy curve confirming the thermodynamic stability at above 192 GPa. The dynamical stability of the $C2/m$ structure can be investigated by inspecting phonon dispersion curves (Figure 2a). No imaginary frequency was found for whole Brillouin zone of the phase $C2/m$, indicating dynamical stability of this phase. Meanwhile, we

noted that the enthalpy curve of the predicted $I41/amd$ structure is very close to that of the $C2/m$ structure (Figure 1). Thus we also considered the phonon dispersions calculations of the $I41/amd$ structure (Figure 2b). Its phonon dispersions showed imaginary frequencies indicating that this phase structure is dynamically unstable.

Figure 1 The calculated enthalpy difference per formula units (f.u.) with respect to the $Pnnm$ as a function of pressure.

Figure 2 Phonon dispersions of (a) $C2/m$ and (b) $I41/amd$ structures at a pressure of 250 GPa.

As is known, the elastic parameters are the fundamental material parameters that describe mechanical behavior of the crystal structure [33]. The mechanical stability of the predicted phase $C2/m$ is investigated by the calculations of elastic properties. The

monoclinic structure $C2/m$ will be mechanically stable if it satisfied the elastic constants criteria, such as [34]:

$$\begin{aligned}
& (C_{11}, C_{22}, C_{33}, C_{44}, C_{55}, C_{66}) > 0, C_{11}+C_{22}+C_{33}+2(C_{12}+C_{13}+C_{23}) > 0 \\
& C_{33}C_{55} - C_{35}C_{35} > 0, C_{44}C_{66} - C_{46}C_{46} > 0, C_{22}+C_{33} - 2C_{23} > 0 \\
& C_{22}(C_{33}C_{55} - C_{35}C_{35}) + 2C_{23}C_{25}C_{35} - C_{23}C_{23}C_{55} - C_{25}C_{25}C_{33} > 0 \\
& \{2(C_{15}C_{25}(C_{33}C_{23} - C_{13}C_{23}) + C_{15}C_{35}(C_{22}C_{13} - C_{12}C_{23}) + \\
& C_{25}C_{35}(C_{11}C_{23} - C_{12}C_{13})) - (C_{15}C_{15}(C_{22}C_{33} - C_{23}C_{23}) + \\
& C_{25}C_{25}(C_{11}C_{33} - C_{13}C_{13}) + C_{35}C_{35}(C_{11}C_{22} - C_{12}C_{12})) + C_{55}g\} > 0 \\
& g = C_{11}C_{22}C_{33} - C_{11}C_{23}C_{23} - C_{22}C_{13}C_{13} - C_{33}C_{12}C_{12} + 2C_{12}C_{13}C_{23}
\end{aligned} \tag{1}$$

Furthermore, the degrees of anisotropy in bonding between atoms in different planes of the predicted HP phase were investigated by the shear anisotropic factors equations [34,35] as:

$$\begin{aligned}
A_1 &= 4C_{44}/(C_{11} + C_{33} - 2C_{13}); \\
A_2 &= 4C_{55}/(C_{22} + C_{33} - 2C_{23}); \\
A_3 &= 4C_{66}/(C_{11} + C_{22} - 2C_{12}).
\end{aligned} \tag{2}$$

Where A_1 , A_2 , and A_3 are anisotropic factors for the $\{100\}$ shear planes between $\langle 011 \rangle$ and $\langle 010 \rangle$ directions, the $\{010\}$ shear planes between $\langle 101 \rangle$ and $\langle 001 \rangle$ directions, and the $\{001\}$ shear planes between $\langle 110 \rangle$ and $\langle 010 \rangle$ directions, respectively. For the isotropic crystal, A_1 , A_2 , and A_3 must equal unity, otherwise, less or greater than unity indicates the degree of anisotropy. The percentage anisotropy in shear A_G and compressibility A_B were estimated according to the following equations [33,35]:

$$A_B = (B_V - B_R)/(B_V + B_R); A_G = (G_V - G_R)/(G_V + G_R) \tag{3}$$

Where B and G are bulk and shear moduli, the subscripts R and V represent the Voigt and Reuss schemes. The calculated elastic constants, modulus, shear anisotropic factors, and percentage anisotropy of the $C2/m$ structure at 250 GPa are tabulated in Table 1. All the calculated elastic constants of the predicted $C2/m$ structure are satisfied the above monoclinic elastic criterion, which confirms the mechanical stability of the predicted phase. Note that the elastic constants have a relation as $C_{22} > C_{33} > C_{11} > C_{13}$, implying that the $C2/m$ structure is stiffer along b direction than a and c as the same as the reported *marcasite* FeS_2 [12]. The highest value of C_{22} supporting the existence of strong atomic bonds between nearest neighbors along $\{010\}$ plane. From Table 1, the $\{100\}$ and $\{010\}$

shear planes showed more elasticity isotropic ($A_1 \approx A_2 \approx 1.0$) than $\{001\}$ shear plane ($A_3 = 0.443$), which reveals the existence of strong bonding atoms along $\{100\}$ and $\{010\}$ planes. Moreover, we noted that $C2/m$ phase possesses very low shear anisotropy comparing with the value of its bulk anisotropy. For more mechanical characteristics investigations of the predicted structure, the elastic parameters such as Bulk modulus B , shear modulus G , Young's modulus Y , Poisson's ν and Pugh's k ratios were calculated. The large values of elastic parameters for $C2/m$ phase structure indicating the sensitivity of these parameters to the pressure. The value of Pugh's modulus is ($k = G/B < 0.57$) revealing the ductile manner of $C2/m$ and at 250 GPa [36].

Table 1

Calculated elastic constants C_{ij} / GPa, bulk moduli (B_V , B_R , B_H)/ GPa, shear modulus G / GPa, Young's modulus Y / GPa, Poisson's ratio ν , Pugh's modulus ratio k , shear anisotropic factors (A_1 , A_2 , A_3), and percentage anisotropy (A_B and A_G) of the HP predicted phase $C2/m$.

Elastic parameters	C ₁₁	C ₂₂	C ₃₃	C ₄₄	C ₅₅	C ₆₆	C ₁₂	C ₁₃	C ₁₅	C ₂₃	C ₂₅	C ₃₅	C ₄₆	
	1525	1963	1644	274	648	269	531	1055	55.2	548	135.7	-126.8	2.1	
Elastic modulus, shear anisotropic factors, and percentage anisotropy	B _V	B _R	B _H	G _V	G _R	G _H	Y	ν	k	A ₁	A ₂	A ₃	A _B	A _G
	767.0	764.6	765.8	232.6	513.5	373.1	1048.79	0.33	0.37	1.034	1.032	0.443	0.0015	-0.376

3.2 Structural and electronic Properties

The detailed structural parameters of the newly predicted $C2/m$ structure are represented in Table 2. At 250 GPa, each Fe has three nearest and three next-nearest neighboring S with distances of 1.98 Å and 2.03 Å, respectively. These Fe-S distances are smaller than reported theoretical calculations of Fe-S at ambient pressure [37,38], due to direct influence of HP on atomic distances [39]. As we will show below, each Fe forms 6 Fe-S bonds with those 6 neighboring S. Each S has six neighbors of three S and three Fe. The near S-S distances in the structure are 1.99 Å and 2.04 Å, nearly identical to twice the covalent radius (1.02 Å) of S. This result supports that each S forms 3 S-S bonds with those 3 neighboring S. Polyhedral views of the $C2/m$ structure and its corresponding electron localization functions (ELF) were shown in Figure 3. It showed that each Fe are six-fold bonded to the S atoms forming the distorted edge-sharing FeS_6 octahedron, while the connectivity pattern of S-S bonds forms two 1D zigzag-like chains along b and c axis, respectively. Analysis of the ELF reveals strong covalent interactions

between near neighbors of Fe and S atoms. The bonding characters are further depicted using calculations of the difference charge density in Figure 4. It clearly shows an increase in the electronic charge around S atoms, with a weak polarization toward Fe atoms where charge depleted, suggesting a mixed ionic-covalent character of the Fe–S bond.

Figure 3 (a) The crystal structures of $C2/m$. (b) Isosurface of ELF at the value of 0.75 of $C2/m$ structure.

Table 2

Structural parameters and Wyckoff positions of $C2/m$ phase at 250 GPa.

Structure	Space group	Unit cell parameters			Wyckoff positions	X	Y	Z
		a / Å	b / Å	c / Å				
FeS ₂ $\alpha = \gamma = 90^\circ$ $\beta = 118.9670$	$C2/m$ unique axis b	6.8857	3.7800	3.9150	Fe 4i	0.13355	- 0.000	0.40239
					S 4i	0.19870	- 0.000	0.96628
					4i	0.03734	0.5	0.28418

Figure 4 The calculated differential charge density, (a) contour map along {010} plane, (b) three dimensions isosurface (section = 0.3) for $C2/m$ phase at 250 GPa.

To investigate the electronic structure of the predicted $C2/m$ structure, we calculated the band structure and electronic densities of state (DOS). Note that several electronic bands crossed Fermi level (Figure. 5) and it possesses metallic feature. This feature mainly arises from the d states of Fe atom indicated by the projected DOS in Figure 6. As shown in Figure 6, the top valence bands are essentially composed of states of p character provided by the S atoms and d character of Fe atoms. The Fe- d and S- p states are present a weak energy degenerate in the top valence bands region. This facilitates the Fe-S hybridization and thus the formation of directionally covalently bonded FeS_6 polyhedron subunits in the structure.

Figure 5 The band structure of $C2/m$ structure at pressure of 250 GPa. The dotted line represents Fermi level.

Figure 6 Total and partial density of states (DOS) of iron and sulfur atoms for $C2/m$ structure.

3.3 Thermoelectric properties

Recently, the natural minerals are reported to be a suitable material for achieving high thermoelectric (TE) efficiency [12,40]. The iron disulfide is one of missionary minerals that attracted attention as a material for use in applications of energy harvesting and conversion [41]. Based on this, the TE properties of the HP phase $C2/m$ are investigated at a pressure of 250 GPa using Boltzmann transport equation [29] and presented at figure 7. The electrical conductivity of the material can be considered as the flow of free electrons due to temperature difference. From figure 7b, the electrical conductivity (σ/τ) increases with increasing temperature (T). At room temperature (RT), σ/τ (where τ is relaxation time) observed at $5.29 \times 10^{20} (\Omega m s)^{-1}$ which is much here than that reported in marcasite and pyrite FeS_2 [12]. As is known, the thermoelectric efficiency is proportional to the figure of merit ($ZT = S^2 \sigma T / \kappa$, where S , σ and κ are seebeck coefficient, electrical conductivity and thermal conductivity, respectively). A material associated with high S and low κ is expected to have a good thermoelectric efficiency [42,43]. The Seebeck coefficient S of $C2/m$ structure was calculated at temperature (T) range 100 – 800K and depicted in Figure 7c. Below room temperature (RT), S changes from negative ($-3.7 \mu V/K$, the majority of charge carriers are electrons) to positive (the majority are holes) and reached the value of $-2.46 \mu V/K$ at 300K. These values are much smaller than previous reports in FeS_2 [12,38]. Due to the low S and high value of κ as shown in Figure 7(a,c), the maximum value of figure of merit ZT is $2.5 \times 10^{-6} / K$ at 210 K, which is smaller than the experimental results in *pyrite*- FeS_2 (about $10^{-5} / K$) [44]. Although σ/τ increases with increasing T, the calculated ZT reveals that $C2/m$ structure possess a weak thermoelectric efficiency.

Figure 7. (a) Seebeck coefficient, (b) figure of merit, (c) electronic thermal conductivity and (d) electrical conductivity for $C2/m$ structure as functions of temperature at 250 GPa.

4. Conclusions

In summary, we have explored the HP structural phase transitions of FeS_2 at 50–300 GPa using crystal structure predictions CALYPSO technique combined with first-principle calculations method. A brand new $C2/m$ structure has been predicted to be stable at above 192 GPa. Its thermodynamical, dynamical and mechanical stability are further verified. Analysis of the electronic structure indicates that the $C2/m$ structure contains of the distorted FeS_6 octahedron and two connected 1D zigzag-like S chains, possessing a good metallic feature. Moreover, the thermoelectric calculations indicate that the electronic thermal conductivity and electrical conductivity of $C2/m$ structure increase with increasing temperature. Meanwhile, it is found that the $C2/m$ phase behaves in a ductile manner through the elastic parameters calculations. This work provides the guidance for further research investigations of FeS_2 under HP.

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