

Density Functional Theory Study on the Electronic Properties of Mg Doped FePS₃

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Abstract

Density functional theory (DFT) calculations have been performed to investigate various electronic and structural properties of FePS₃ doped with Mg using the plane wave pseudopotential method as implemented in the Quantum Espresso code. The electronic conductivities of Fe₃Mg₁P₄S₁₂, Fe₄P₃Mg₁S₁₂ and Fe₄P₄S₁₁Mg₁ were evaluated in terms of density of states (DOS). Their electronic state at the Fermi level indicates that Fe₃Mg₁P₄S₁₂, and Fe₄P₄S₁₁Mg₁ exhibit a non-metallic behavior. While the electronic state for Fe₄P₃Mg₁S₁₂ shows a metallic behavior. Structural analysis indicate that the alloy Fe₃Mg₁P₄S₁₂ has the highest adsorption. The stability and electronic conductivity make these alloy promising material for Magnesium ion batteries (MIB).

Keywords: Density functional theory, pseudopotential, adsorption, density of state, Magnesium ion.

1. Introduction

Batteries are the most commonly used storage devices and the lithium-ion battery is the most commercialized and generally used battery type in the industry. However, the recent speedy development of society requires a major improvement in battery materials to achieve high capacity, long life cycle, low cost and reliable batteries. As a result, numerous energy-efficient storage materials and battery systems are being investigated, and their operating processes must be fully understood before they can be used in industry. Density Functional Theory (DFT) has been used to the subject of energy storage in recent years, and it has made significant advances to the understanding of electrochemical reaction processes and virtual screening of prospective energy storage materials.

As the need for energy sources grows, so does the usage of finite nonrenewable fossil fuels, resulting in a growing number of environmental issues. Researchers concentrated on renewable energies and effective energy storage to address this pressing issue [1]. Lithium-ion batteries (LiBs) have been widely used in scalable energy storage systems, electric vehicles, and portable electronic gadgets as one of the most successful energy storage technologies [2].

Gin Lewis originally developed the ideal Lithium-ion battery in 1912, but it wasn't practicable until the 1970s, and it wasn't commercialized until the 1980s. Engineers attempted and partially succeeded in creating the first rechargeable battery using lithium as the material. They failed to notice, however, that these batteries were unstable throughout the charging process, resulting in a short inside the battery, which increased the temperature and caused thermal runaway. After significant research, Sony developed superior Li-ion batteries with novel chemistry, which are still in use today.

Despite the fact that LIBs have advanced and are now widely available rechargeable batteries, they have not been recognized as acceptable long-term energy storage technology due to Lithium's high cost, unavailability, and safety concerns [3]. Because of their low cost, safety, and natural abundance, magnesium-ion batteries (MIBs) are gaining popularity. Mg (\$3/kg) has a lower price than Li (\$185/kg), yet Mg reserves in the crust (2.33%) are around 350 times larger than Li (0.0065%) [4,5]. Furthermore, MIBs have an advantage in the electrochemical process. Because of the divalent nature of magnesium, its theoretical volumetric capacity (3832

mA h/cm³) is higher than that of lithium (2062 mA h/cm³) [6]. Second, dendrite is a serious problem for lithium metal anodes, whereas magnesium metal used as an anode can achieve dendrite-free depositing during cycling, resulting in a comparatively safe cycling process [7]. As a result, MIBs could be a viable alternative to LIB technology. However, continual electrolyte consumption and the reactivity of Mg metal with electrolyte interfaces (SEI). Slow insertion/extraction reaction kinetics are caused by sluggish Mg ions in the host material due to the divalent nature of the mg ion.

Commercially available battery made from Lithium-ion are expensive and has a low volumetric capacity. Much is not known about the insertion reaction kinetics of Mg-ion (a possible alternative to the expensive Lithium-ion) into the transition metal trichalcogenides (FePS₃).

2. Computational Methods

As illustrated in figure 2.1(a), FePS₃, a standard MPX₃ material, crystallizes in a monoclinic structure with space group C2/m (No. 12) and lattice parameters a=5.858 Å, b=10.361 Å, c=7.086 Å. Because of its huge specific surface area, plentiful active sites, and quick ion diffusion, it is projected to be a suitable anode for MIBs. FePS₃ has a moderate electronic conductivity of 10⁻⁵ S/cm, which is much greater than the electronic conductivity of other MPX₃ materials including MnPS₃, NiPS₃, and ZnPS₃ (about 10⁻⁹ S/cm). Density functional theory (DFT) computations were used to investigate Mg adsorption and electronic properties in a FePS₃ alloy, which could be used as an anode candidate for MIBs.

All the calculations were carried out in the Materials Square web-based simulation platform [8] using the Quantum Espresso Package [9] to simulate and analyze the FePS₃ before and after it was doped with Magnesium to get the Density of State (DOS), band structure and band gap. The Ultrasoft pseudopotential was adopted to describe the core-valence interaction, and the exchange-correlation functional is in the form of Perdew-Bruke-Ernzerhof (PBE) with the generalized gradient approximation (GGA). A kinetic energy cut-off for wavefunctions of 50 Rydberg, a convergence threshold for self-consistency of 10⁻⁶ Rydberg was used. Structural relaxations were done with a 9 x 7 x 8 k-mesh while their electronic structure properties were calculated using a 10 x 6 x 8 k-mesh and a Gaussian smearing width of 0.002 for the occupation. The structure was optimized before and after the insertion of Mg impurity atoms, then band structure as well as DOS calculations were done. An Mg atom was initially placed at the Fe sites (see figure 2.1(b)), then in the P sites (see figure 2.1(c)) and in the S site (see figure 2.1(d)) of the FePS₃ crystal.

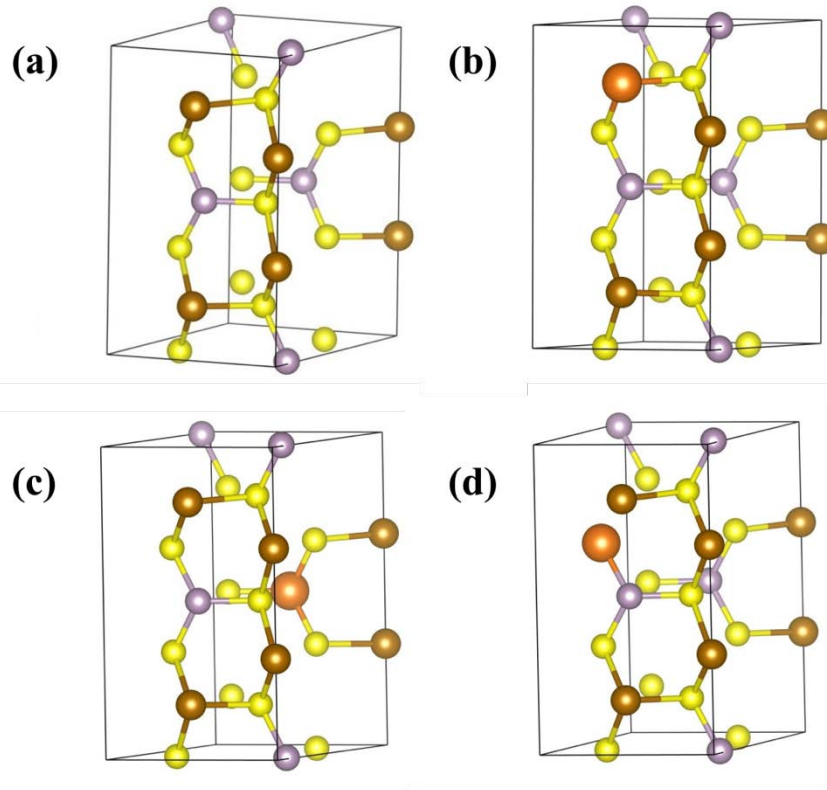


Figure 2.1. (a) Crystal structure of bulk FePS_3 . (b) Impurity model of Mg doped FePS_3 with Mg inserted in the Fe site. (c) Impurity model of Mg doped FePS_3 with Mg inserted in the P site. (d) Impurity model of Mg doped FePS_3 with Mg inserted in the S site. Where the Fe, P, S and Mg atoms are represented with Brown, purple, yellow and orange spheres respectively.

3. Results and Discussions

3.1 Bulk FePS_3

This work started with the relaxation of FePS_3 ($\text{Fe}_4\text{P}_4\text{S}_{12}$) and band structure as well as density of state (DOS) calculations was performed for the bulk system FePS_3 . Figure 3.1 (a) gives the DOS plot for FePS_3 . The dip at the Fermi level is an indication of the band gap in this compound and the number of states here is approximately zero. For the band structure computation, we got a band gap energy of 0.24 eV as shown in figure 3.2 (a), which is close to the value of 0.22 eV gotten in other DFT calculations [10]. As can be seen from the band structure diagram, FePS_3 has an indirect band gap with the valence band maximum (VBM) at the gamma point and conduction band minimum (CBM) at the X point along the wave vector axis.

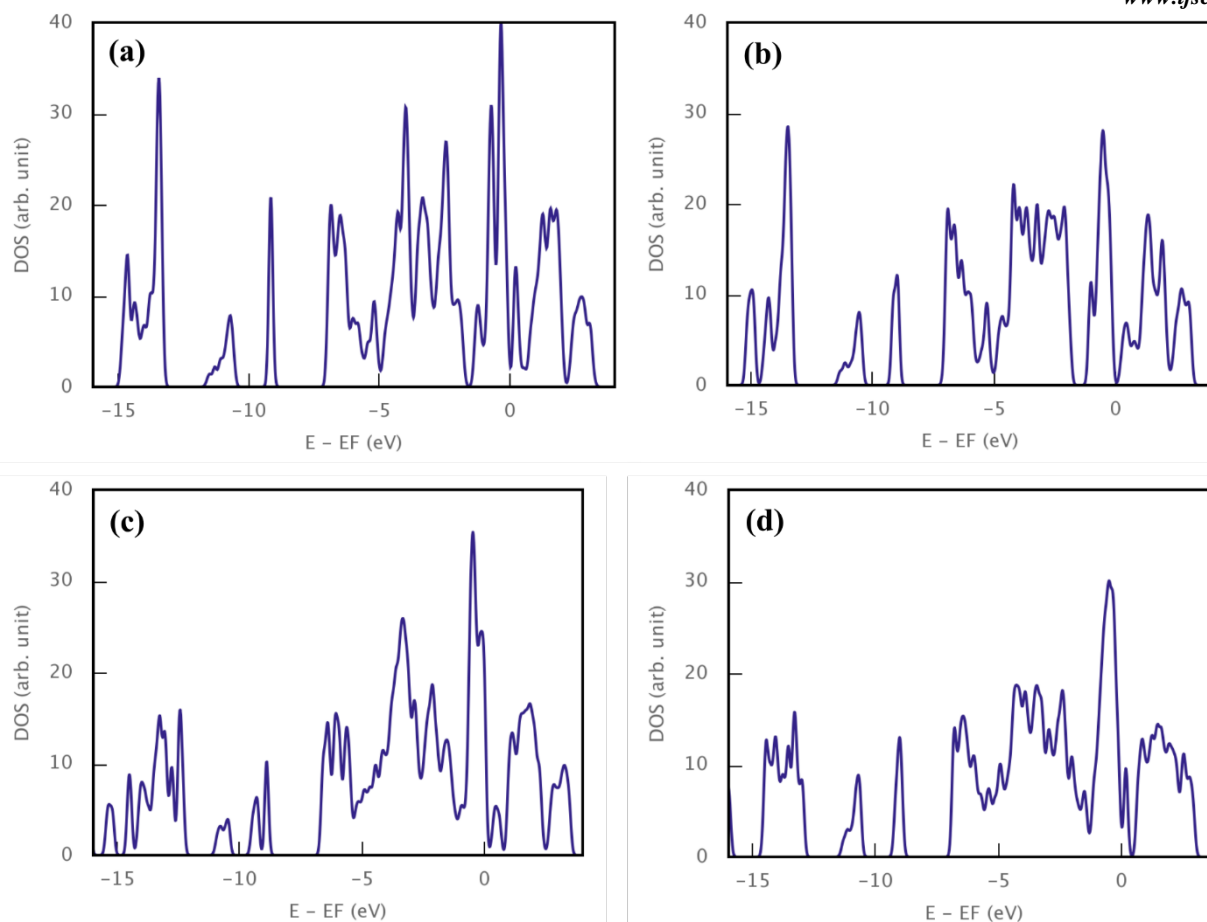


Figure 3.1. (a) Density of state plot for bulk FePS₃. (b) DOS plot for Mg doped FePS₃ with Mg inserted in the Fe site. (c) DOS plot for Mg doped FePS₃ with Mg inserted in the P site. (d) DOS plot for Mg doped FePS₃ with Mg inserted in the S site.

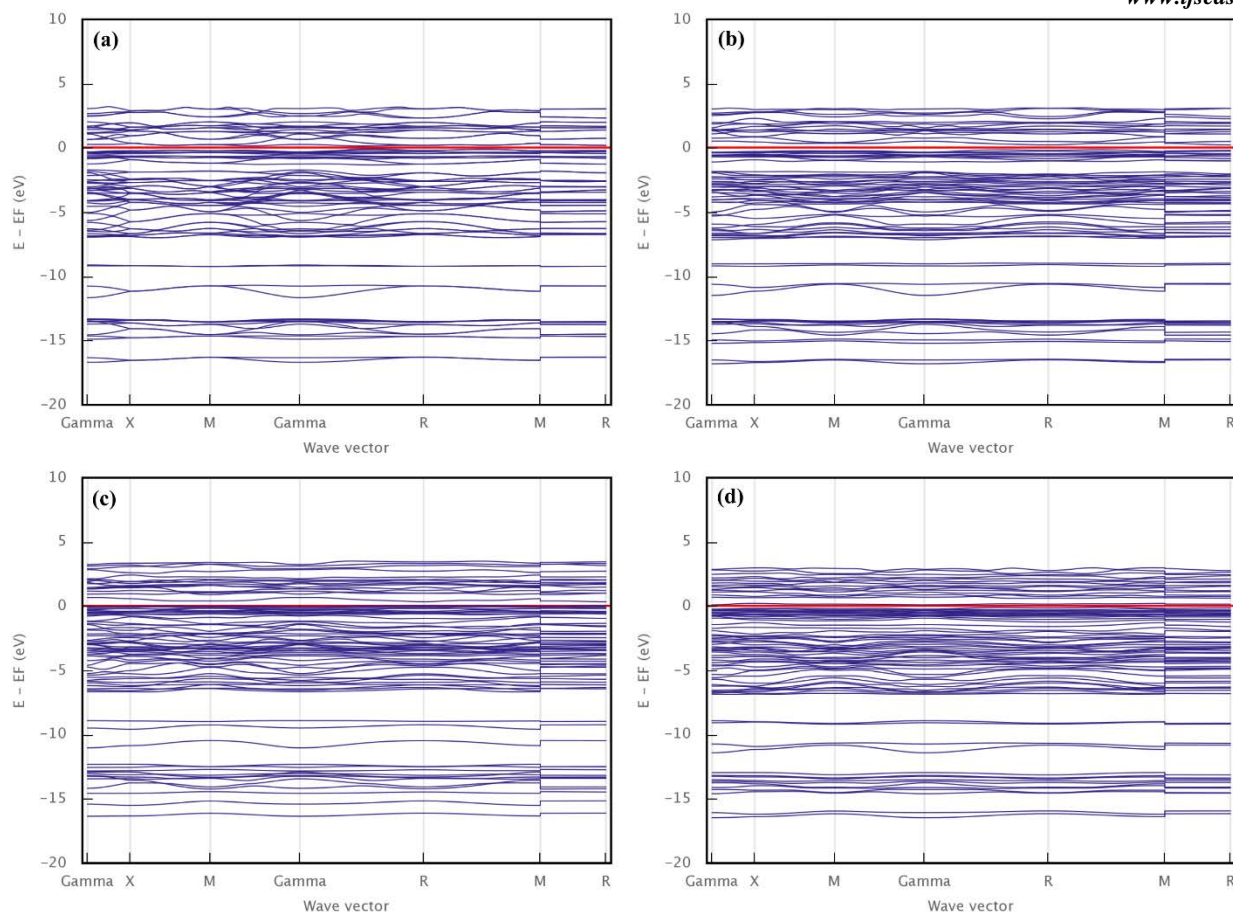


Figure 3.2 (a) Band structure of bulk FePS_3 (b) Band structure plot for Mg doped FePS_3 , with Mg inserted in the Fe site. (c) Band structure plot for Mg doped FePS_3 , with Mg inserted in the P site. (d) Band structure plot for Mg doped FePS_3 , with Mg inserted in the S site.

3.2 Mg Doped FePS_3

After the relaxation of the Mg doped FePS_3 models, their density of state properties was calculated to ascertain the number of electronic states available at the Fermi Level. When the Mg impurity is inserted into the Fe, P and S site, the alloys formed are $\text{Fe}_3\text{Mg}_1\text{P}_4\text{S}_{12}$, $\text{Fe}_4\text{P}_3\text{Mg}_1\text{S}_{12}$ and $\text{Fe}_4\text{P}_4\text{S}_{11}\text{Mg}_1$ respectively (see figures 2.1 (b-d)). An important parameter affecting the electrochemical performance of rechargeable batteries is the electronic conductivity of electrode materials. The electronic conductivities of $\text{Fe}_3\text{Mg}_1\text{P}_4\text{S}_{12}$, $\text{Fe}_4\text{P}_3\text{Mg}_1\text{S}_{12}$ and $\text{Fe}_4\text{P}_4\text{S}_{11}\text{Mg}_1$ were evaluated in terms DOS as shown in figures 3.1(b) through (d), respectively. The electronic state at the Fermi level is near zero for $\text{Fe}_3\text{Mg}_1\text{P}_4\text{S}_{12}$, and $\text{Fe}_4\text{P}_4\text{S}_{11}\text{Mg}_1$, (figures 3.1 (b) and (d)), indicating that they exhibit a non-metallic behavior. While the electronic state for $\text{Fe}_4\text{P}_3\text{Mg}_1\text{S}_{12}$ (figures 3.1 (c)) is not zero, indicating a metallic behavior.

Figures 3.2 (b), (c), and (d) respectively depicts the band structure of $\text{Fe}_3\text{Mg}_1\text{P}_4\text{S}_{12}$, $\text{Fe}_4\text{P}_3\text{Mg}_1\text{S}_{12}$ and $\text{Fe}_4\text{P}_4\text{S}_{11}\text{Mg}_1$ with their bandgaps given in table 1. The band gap of $\text{Fe}_4\text{P}_3\text{Mg}_1\text{S}_{12}$ is zero, which is smaller than that of bulk FePS_3 and other alloys, indicating that the insertion of Mg ion in the P site of bulk FePS_3 can improve electronic conductivity. However, inserting Mg into the Fe site of bulk FePS_3 increases the band gap to 0.37 eV and adding more Mg atoms (x) results in further increment in the band gap of the $\text{Fe}_{4-x}\text{Mg}_x\text{P}_4\text{S}_{12}$ alloy system (x is the number of Mg atoms).

The Mg adsorption properties in bulk FePS_3 were evaluated for the alloy systems $\text{Fe}_3\text{Mg}_1\text{P}_4\text{S}_{12}$, $\text{Fe}_4\text{P}_3\text{Mg}_1\text{S}_{12}$, and $\text{Fe}_4\text{P}_4\text{S}_{11}\text{Mg}_1$ using the change in bond length after structural optimization. With Mg is inserted into the Fe site, the bond distance increases slightly by 2.38 %. While for the other systems where Mg was inserted into the P and S sites, the bond length increases by over 27 % as shown in table 1. This slight increase in bond length for the $\text{Fe}_3\text{Mg}_1\text{P}_4\text{S}_{12}$ alloy means that an attraction (adsorption) takes place between the Mg and neighboring S atoms. The large increase in bond length for the $\text{Fe}_4\text{P}_3\text{Mg}_1\text{S}_{12}$, and $\text{Fe}_4\text{P}_4\text{S}_{11}\text{Mg}_1$ alloys signifies a repulsion between Mg and neighboring S (P) atoms. Bulk FePS_3 as well as the alloy systems $\text{Fe}_3\text{Mg}_1\text{P}_4\text{S}_{12}$, $\text{Fe}_4\text{P}_3\text{Mg}_1\text{S}_{12}$, and $\text{Fe}_4\text{P}_4\text{S}_{11}\text{Mg}_1$ exhibits an A–A stacking model after structure relaxation. The highest Mg adsorption corresponds to the formula of $\text{Fe}_3\text{Mg}_1\text{P}_4\text{S}_{12}$ which is in agreement with the work of Cao *et al.* [11].

Table 1: Band gaps and Bond lengths for the different Mg doped FePS_3 alloy systems.

Alloy System	Band Gap (eV)	Bond Type	Bond Length (Å)		
			Before Optimization	After Optimization	Percentage Increase (%)
$\text{Fe}_3\text{Mg}_1\text{P}_4\text{S}_{12}$	0.37	Mg-S	2.52	2.58	2.38
$\text{Fe}_4\text{P}_3\text{Mg}_1\text{S}_{12}$	0.00	Mg-S, Mg-P	2.04, 2.20	2.60, 3.07	27.45, 39.55
$\text{Fe}_4\text{P}_4\text{S}_{11}\text{Mg}_1$	0.18	Mg-P	2.05	2.68	30.73

4. Conclusions

In this work, DFT calculations were conducted to investigate various structural and electronic properties of FePS_3 doped with Mg using the plane wave pseudopotential method as implemented in the Quantum Espresso code. The electronic properties were analysed in terms of the density of states and band structure for the various impurity models ($\text{Fe}_3\text{Mg}_1\text{P}_4\text{S}_{12}$, $\text{Fe}_4\text{P}_3\text{Mg}_1\text{S}_{12}$, and $\text{Fe}_4\text{P}_4\text{S}_{11}\text{Mg}_1$). Results from the DFT calculations shows that when Mg is inserted into the Fe site of FePS_3 , the most stable alloy ($\text{Fe}_3\text{Mg}_1\text{P}_4\text{S}_{12}$) was formed in comparison to the other alloy systems. $\text{Fe}_3\text{Mg}_1\text{P}_4\text{S}_{12}$ show a non-metallic behaviour with a small band gap of 0.37 eV and this band gap can be enhanced by increasing the number of Mg atoms added to the Fe site. Insertion of Mg into FePS_3 exhibit good electronic conductivity (as seen in the case of the alloy $\text{Fe}_4\text{P}_3\text{Mg}_1\text{S}_{12}$), which are beneficial to cycling stability and high-rate performance of a battery. FePS_3 is a suitable anode material for Mg ion batteries because it can provide a relatively low voltage, contributing a high-power density in full batteries. Also, Mg can be inserted at the Fe sites in FePS_3 with a stable structure as in the case of $\text{Fe}_3\text{Mg}_1\text{P}_4\text{S}_{12}$ which has the largest adsorption energy.

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