Calculation of Electronic Structures and Magnetic Properties of α-quartz SiO_2 with and without Transition Metal Elements

การคำนวณโครงสร้างอิเล็กทรอนิก และคุณสมบัติทางแม่เหล็ก ของอัลฟา-ควอทร์ซ ซิลิกาที่เจือด้วยโลหะแทรนซิชัน

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Abstract

Electronic structures and magnetic properties of pure α-quartz SiO_2 and doped α-quartz $Si_{1-x}M_xO_2$, where M represents the transition metals V, Cr and Mn, are calculated using the Gaussian98 program with the Hartree-Fock (HF) and Density Functional Theory (DFT) methods. In this calculation $Si_{18}O_{26}H_{32}$ and $Si_{17}MO_{26}H_{32}$ represent pure and doped α-quartz SiO_2 respectively. The total energy calculated by DFT is found to be smaller than that calculated by HF and the lowest is found in $Si_{17}MnO_{26}H_{32}$. The results show that the energy gaps of $Si_{18}O_{26}H_{32}$ calculated by HF and DFT methods are 15.766 eV and 7.560 eV respectively. The energy gaps of doped α-quartz SiO_2 calculated by both methods, are found to reduce and the narrowest one is found in $Si_{17}CrO_{26}H_{32}$. The calculations of the total dipole moments show that these values are higher in doped α-quartz SiO_2 than in pure α-quartz SiO_2, while the highest is found in $Si_{17}MnO_{26}H_{32}$.

บทคัดย่อ

งานวิจัยนี้ได้ทำการคำนวณโครงสร้างอิเล็กทรอนิก และสมบัติทางแม่เหล็กของอัลฟา-ควอทร์ซ ซิลิกา (α-quartz SiO_2) บริสุทธิ์และที่เจือด้วยโลหะแทรนซิชัน V, Cr และ Mn โดยใช้โปรแกรม Gaussian 98 ซึ่งได้ทำการคำนวณโดยวิธี Hartree-Fock (HF) และวิธี Density Functional Theory (DFT) ในการคำนวณนี้ได้ใช้ $Si_{18}O_{26}H_{32}$ แทนอัลฟา-ควอทร์ซ ซิลิกาบริสุทธิ์ และ $Si_{17}MO_{26}H_{32}$ แทนอัลฟา-ควอทร์ซ ซิลิกาที่เจือด้วยโลหะแทรนซิชัน ผลที่ได้จากการคำนวณพบว่าค่าพลังงานรวมที่ได้จากวิธี Density Functional Theory (DFT) จะมีค่าน้อยกว่าค่าพลังงานรวมที่ได้จากวิธี Hartree-Fock (HF) สำหรับทุกๆ โครงสร้าง โดยโครงสร้างของ $Si_{17}MnO_{26}H_{32}$ มีค่าพลังงานรวมต่ำที่สุด นั่นคือ มีความเสถียรมากที่สุด และเมื่อวิเคราะห์หาค่า energy gap พบว่าค่า energy gap ของโครงสร้าง $Si_{18}O_{26}H_{32}$ ที่ได้จากการคำนวณโดยวิธี HF และ DFT มีค่าเท่ากับ 15.766 eV และ 7.560 eV ตามลำดับ แต่เมื่อเจือด้วยโลหะแทรนซิชัน พบว่า ค่า energy gap ที่ได้จากการคำนวณทั้ง 2 วิธีมีค่าลดลง โดยโครงสร้าง $Si_{17}CrO_{26}H_{32}$ มีค่า energy gap น้อยที่สุด จากการคำนวณค่าไดโพลโมเมนต์รวม (Total dipole moment) พบว่าอัลฟา-ควอทร์ซ ซิลิกาที่เจือด้วยโลหะแทรนซิชัน มีค่าไดโพลโมเมนต์รวมเพิ่มขึ้นจากอัลฟา-ควอทร์ซ ซิลิกาบริสุทธิ์ โดย $Si_{17}MnO_{26}H_{32}$ มีค่าไดโพลโมเมนต์รวมมากที่สุด

Keywords: Electronic structure, total dipole moment, α-quartz SiO_2
คำสำคัญ: โครงสร้างอิเล็กทรอนิก ผลรวมของค่าไดโพลโมเมนต์ อัลฟา-ควอทร์ซ ซิลิกา

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Introduction

Silica, SiO_2, in both amorphous and crystal forms is a very well-known material that is used worldwide due to its application in various fields such as cosmetics, drugs, foods, ceramic and glass industries, optical fibers, catalysis and microelectronics. General data and some details of silica's properties and its derivatives can be found in many textbooks in chemistry and materials science. Moreover, there is also a special monograph on silica (Devine et al., 2000) and a vast number of research articles. In general, silica is an insulator or semiconductor depending on its crystal structure and the width of the energy gaps. In addition, silica itself is not a ferromagnetic material. Recently, however, a study of its electronic structure and magnetic properties suggest that silica might be useful for spintronic (or spin-based electronics) applications (Wolf et al., 2001). In this technique, the spin of the electron carries information that can be used as an added degree of freedom in novel electronic devices. Thus, the development of functional ferromagnetic semiconductors is a key to the development of spintronic devices that will certainly be devices utilized in the future. Magnetic semiconductors based on non-magnetic semiconductors are so called dilute magnetic semiconductors (DMS).

There are some theoretical studies of α-quartz SiO_2 doped with some transition metals and non-transition metals which reveal that these materials can show ferromagnetic properties at room temperature (Dihn et al., 2005). In this work the electronic structures and total magnetic moments of pure α-quartz SiO_2 and doped α-quartz SiO_2 with Mn, V and Cr have been calculated using Hatree Fock (HF) and Density Functional Theory (DFT) methods (Jensen, 1988).

Structure of α-quartz SiO_2

The structure of α-quartz SiO_2 is described by the space group $P3_221$ and its hexagonal primitive vectors are: $\vec{A}_1 = \frac{1}{2}a\hat{e}_x - \frac{1}{2}\sqrt{3}a\hat{e}_y$, $\vec{A}_2 = \frac{1}{2}a\hat{e}_x + \frac{1}{2}\sqrt{3}a\hat{e}_y$, $\vec{A}_3 = c\hat{e}_z$.

Table 1 shows the coordinates of Si and O in α-quartz SiO_2 structure consisting of 18 Si and 26 O. The structures of $Si_{18}O_{26}$ and $Si_{18}O_{26}H_{32}$ are shown in Figure 1(a) and Figure 1(b) respectively.

Material and Methods

The study of electronic structures and the magnetic properties of pure and doped α-quartz SiO_2 were based on ab initio calculations, Hartree-Fock (HF) and Density Functional Theory (DFT) methods. The Gaussian basis set used in these calculations was 6-31G* for both methods. According to this calculation, we used the structure of $Si_{18}O_{26}H_{32}$ as pure α-quartz and $Si_{17}MO_{26}H_{32}$ as doped α-quartz in which M were V, Cr and Mn. The calculation yielded the density of states (DOS) and the total dipole moment of each α-quartz SiO_2 structure. The GAUSSIAN98 package (Frisch et al., 1998) was used for all calculations. The flowchart of the calculation is shown in Figure 2.

Results and Discussion

Part 1 Calculation of the density of states and energy gap

Figures 3 to 6 illustrate the relationship between density of states and energy of different SiO_2 structures. Each figure depicts a plot of the density of state as a function of energy calculated by the Hatree Fock Method (HF).

Figures 7 to 10 depict plots of the density of states as a function of the energy calculated by the Density Functional Theory Method (DFT).

From Figures 3 to 10, the energy gaps of pure α-quartz SiO_2 and doped α-quartz $Si_{1-x}M_xO_2$ can be calculated by the HF and DFT methods as summarized in Table 2.

From Table 2 it can be seen that the calculation by the DFT method yielded values of E_g smaller than those calculated by the HF method. The E_g of doped α-quartz SiO_2 was reduced in comparison to pure α-quartz SiO_2. This decrease in E_g should result from the creation of localized states due to transition metals in the gap.

Part 2 Calculation of the total dipole moments

Table 3 shows the values of total dipole moment for each SiO_2 structure calculated by the HF and DFT methods. These values could refer to the magnetic properties of each SiO_2 structure.

From Table 3 it can be seen that the total dipole moments of doped α-quartz $Si_{1-x}M_xO_2$ are higher than those for pure α-quartz SiO_2 except in the structure doped by V. Moreover, the highest value of total dipole moment is found in $Si_{17}MnO_{26}H_{32}$. From these results, it is expected that α-quartz SiO_2 could be ferromagnetic after doping with some transition metals.

Conclusions

We have used the HF and DFT methods to calculate the energy gaps, the density of states and the total dipole moments of α-quartz SiO_2 and doped α-quartz $Si_{1-x}M_xO_2$. The energy gaps of doped α-quartz $Si_{1-x}M_xO_2$ calculated by both HF and DFT methods are found to reduce as compared to the pure SiO_2 and the narrowest is found in $Si_{17}CrO_{26}H_{32}$. The total dipole moments of doped α-quartz SiO_2 are higher than those of pure α-quartz SiO_2 except for doping with V. In addition, the highest value of total dipole moment is found in $Si_{17}MnO_{26}H_{32}$. The results confirm that it is possible to induce ferromagnetism in pure α-quartz SiO_2 doped with some transition metals such as Mn, V and Cr.

Acknowledgements

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Table 1. The coordinates of Si and O in α-quartz SiO_2 structure used in this study.

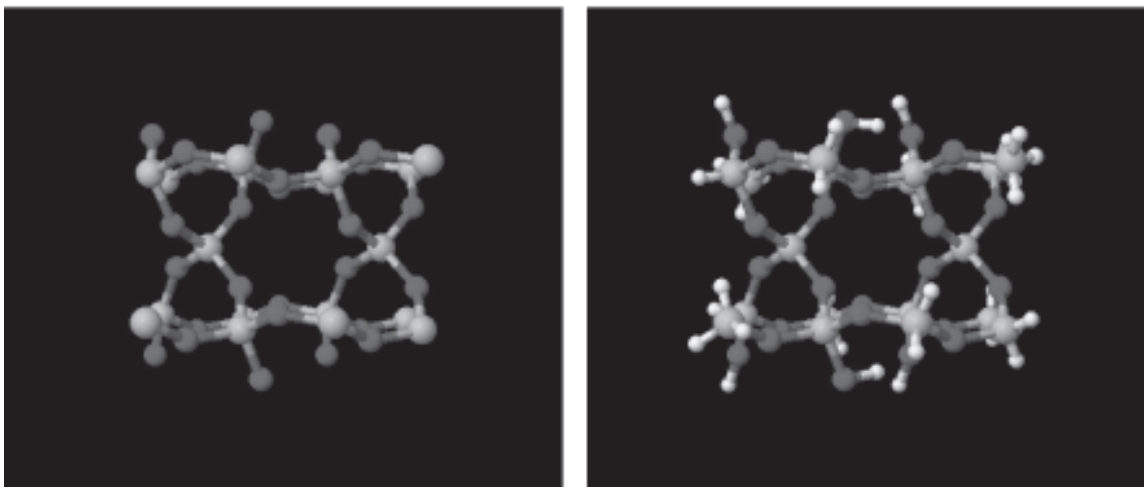
Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
Si	-3.7590	-1.9995	-1.8017	O	-2.7567	-2.4931	2.4435	O	-0.3000	-1.7620	2.9617
Si	-3.7590	1.9995	-3.6035	O	-3.8327	-3.1143	-0.6418	Si	3.6111	2.2556	-1.8017
O	-3.2374	-0.6212	-1.1600	O	-0.7807	-3.6339	1.1600	O	1.0807	3.1143	0.6418
Si	-3.7590	-1.9995	3.6035	Si	1.1544	-1.9995	-1.8017	O	2.1567	2.4931	-2.4435
Si	-3.7590	1.9995	1.8017	Si	1.1544	1.9995	-3.6035	O	2.1567	2.4931	2.9617
O	-3.2374	0.6212	1.1600	O	1.6760	-0.6212	-1.1600	Si	3.6111	-2.2556	-3.6035
Si	-1.3023	2.2556	-1.8017	O	-0.3000	1.7620	-2.9617	Si	3.6111	-2.2556	-3.6035
O	-0.7807	3.6339	-1.1600	Si	1.1544	-1.9995	3.6035	Si	3.6111	-2.2556	1.8017
Si	-1.3023	2.2556	3.6035	Si	1.1544	1.9995	1.8017	O	2.1567	-2.4931	-2.9617
O	-3.8327	3.1143	0.6418	Si	-2.3088	0.0000	0.0000	O	2.1567	-2.4931	2.4435
O	-2.7567	2.4931	-2.4435	O	-0.3000	1.7620	2.4435	O	1.0807	-3.1143	-0.6418
O	-2.7567	2.4931	2.9617	O	-1.3760	-1.1408	0.6418	Si	2.6046	0.0000	0.0000
Si	-1.3023	-2.2556	-3.6035	O	-1.3760	1.1408	-0.6418	O	3.5374	-1.1408	0.6418
O	-2.7567	-2.4931	-2.9617	O	-0.3000	-1.7620	-2.4435	O	3.5374	1.1408	-0.6418
Si	-1.3023	-2.2556	1.8017	O	1.6760	0.6212	1.1600				

Table 2. The Energy gaps of pure and doped α-quartz SiO_2 calculated by HF and DFT methods.

Structure	Energy gap (eV), E_g	
	HF method	DFT method
$Si_{18}O_{26}H_{32}$	15.766	7.560
$Si_{17}VO_{26}H_{32}$	4.359	1.760
$Si_{17}CrO_{26}H_{32}$	10.074	1.263
$Si_{17}MnO_{26}H_{32}$	10.062	3.091

Table 3. The values of total dipole moments of each SiO_2 structure calculated by HF and DFT methods.

Structure	Total dipole moment (Debye)	
	HF method	DFT method
$Si_{18}O_{26}H_{32}$	4.0479	3.6332
$Si_{17}VO_{26}H_{32}$	3.5726	2.7683
$Si_{17}CrO_{26}H_{32}$	4.7830	4.3398
$Si_{17}MnO_{26}H_{32}$	5.1349	4.5009



(a) (b)

Figure 1. The structures of $Si_{18}O_{26}$ (a) and $Si_{18}O_{26}H_{32}$ (b).

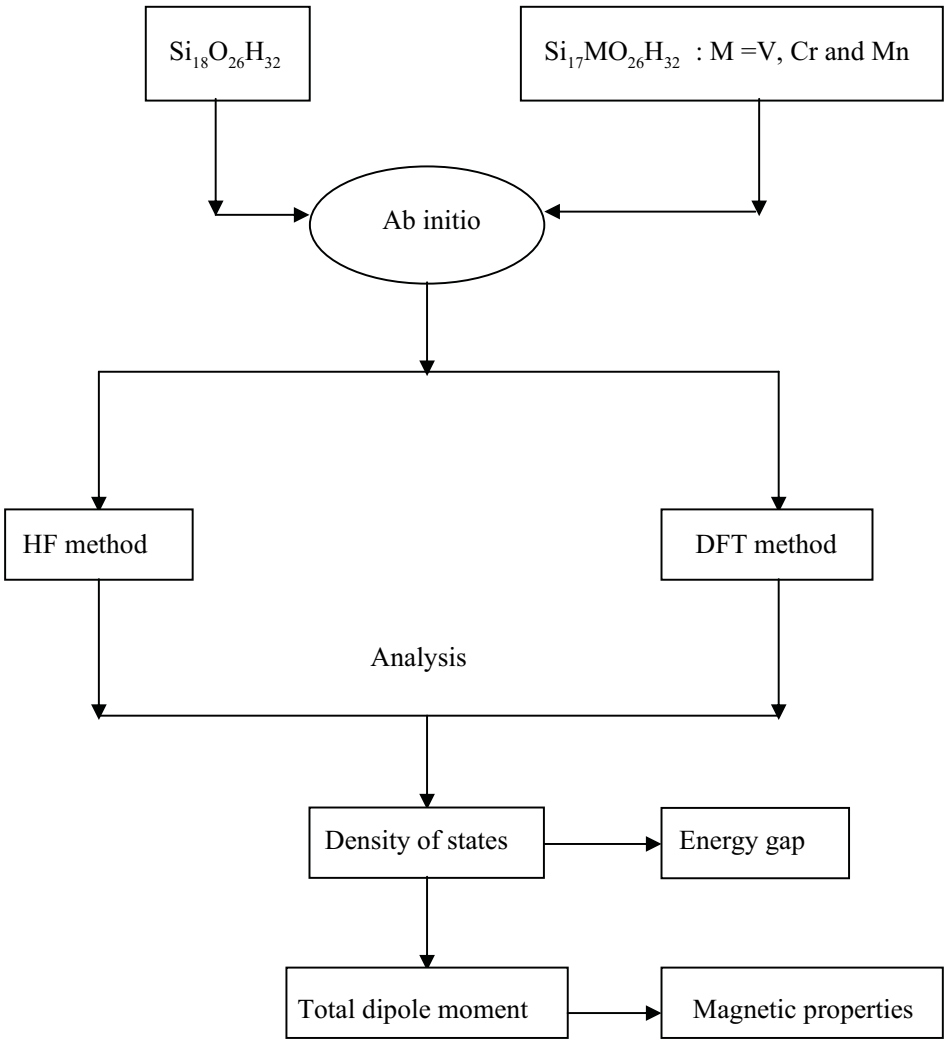


Figure 2. Flowchart for the calculation of the density of states and the total dipole moment of pure and doped α-quartz SiO_2 based on HF and DFT methods (Kidkhunthod, 2006).

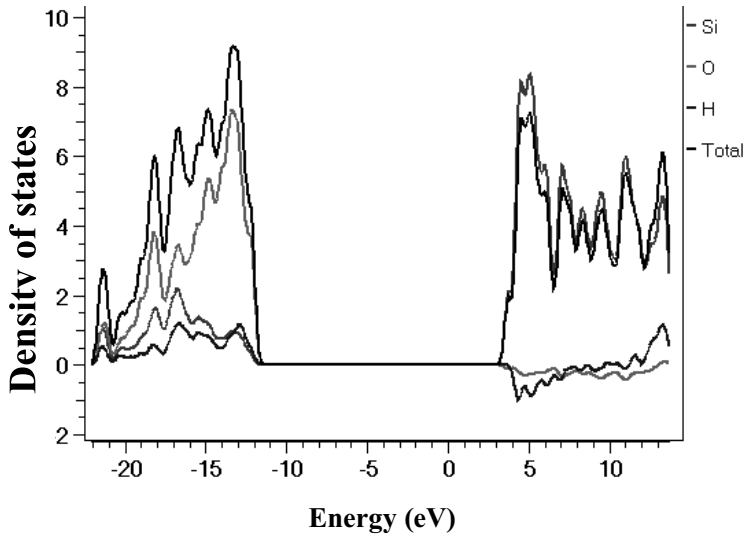


Figure 3. Plot of the density of state versus the energy of $Si_{18}O_{26}H_{32}$ structure using HF method.

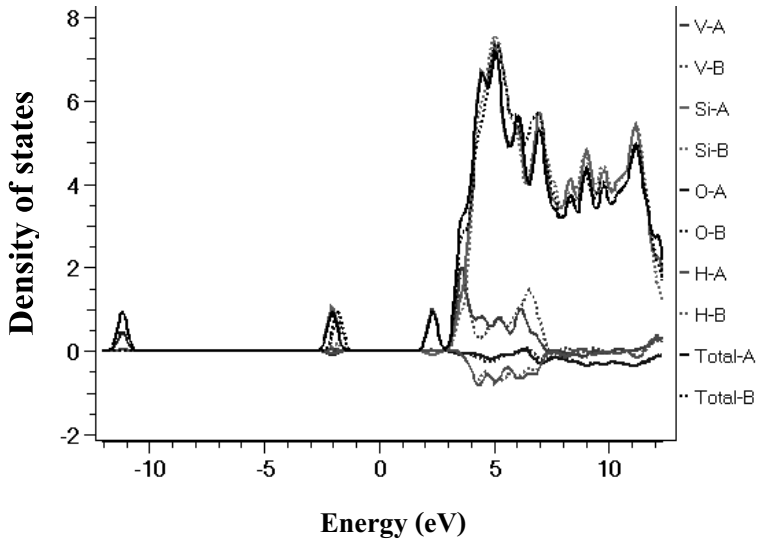


Figure 4. Plot of the density of state versus the energy of $Si_{17}VO_{26}H_{32}$ structure using HF method. A is alpha state of electron and B is beta state of electron.

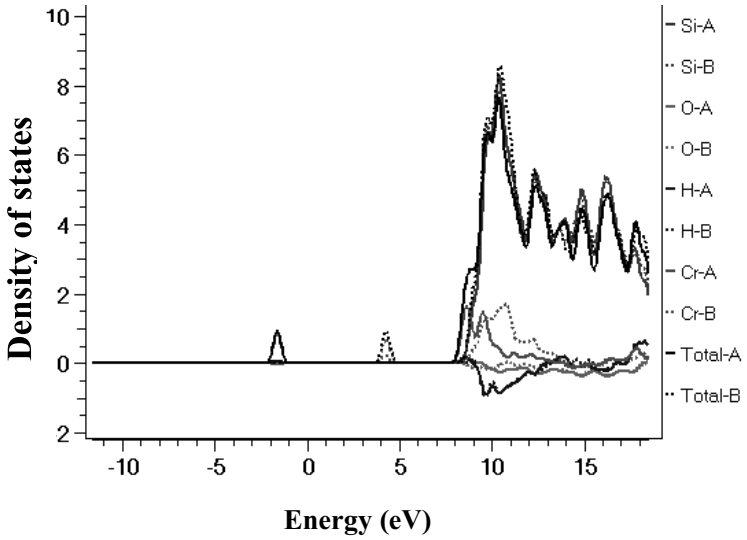


Figure 5. Plot of the density of states versus the energy of $Si_{17}CrO_{26}H_{32}$ structure using HF method.

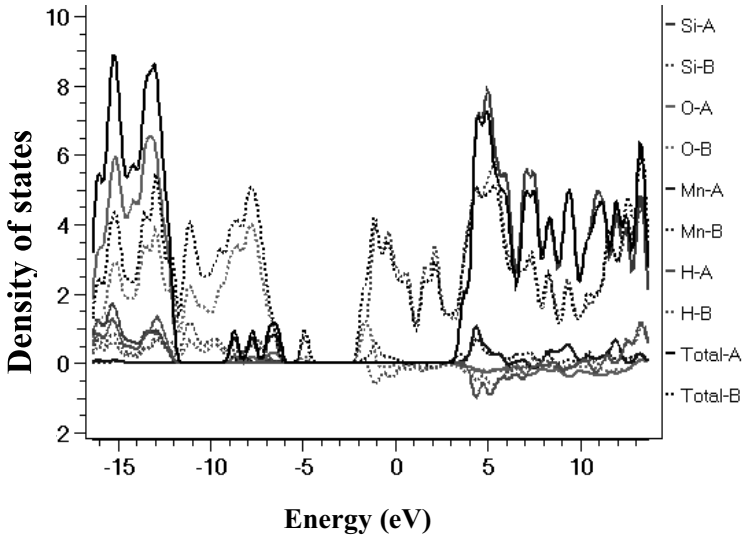


Figure 6. Plot of the density of states versus the energy of $Si_{17}MnO_{26}H_{32}$ structure using HF method.

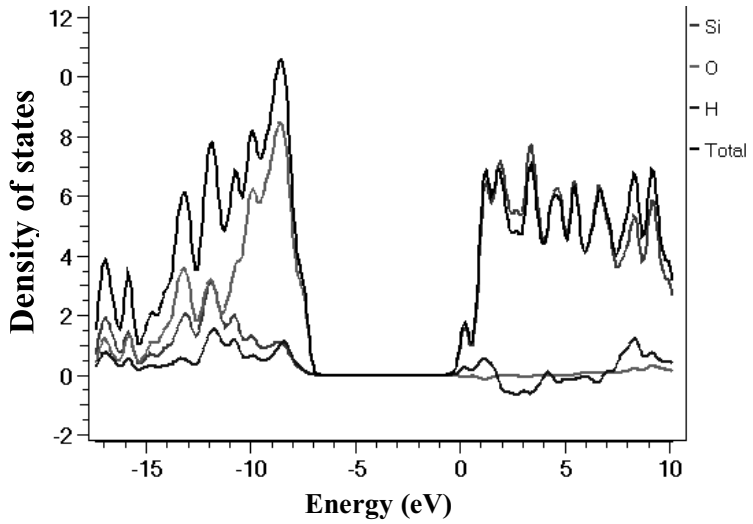


Figure 7. Plot of the density of states versus the energy of $Si_{18}O_{26}H_{32}$ structure using DFT method.

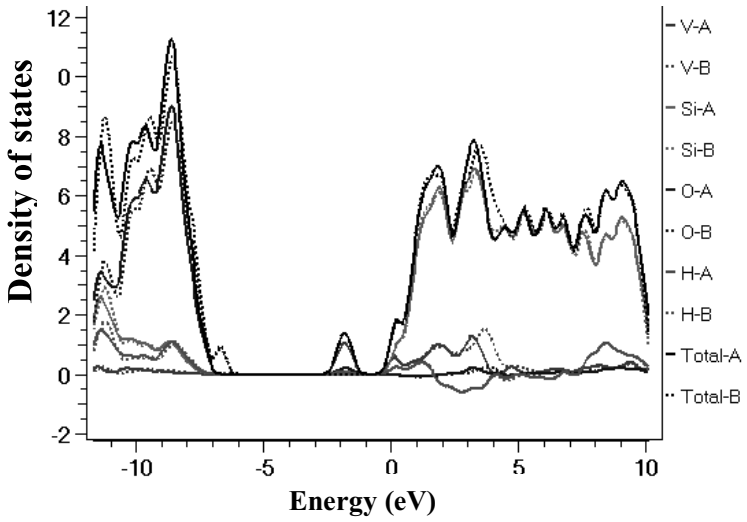


Figure 8. Plot of the density of states versus the energy of $Si_{17}VO_{26}H_{32}$ structure using DFT method.

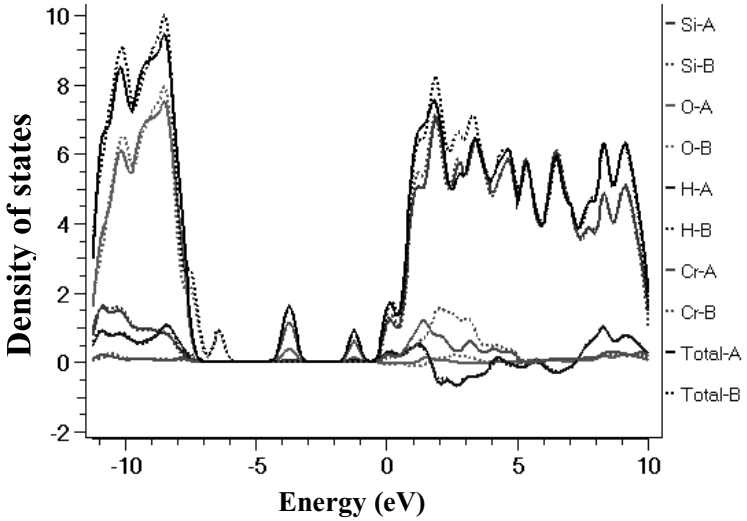


Figure 9. Plot of the density of states versus the energy of $Si_{17}CrO_{26}H_{32}$ structure using DFT method.

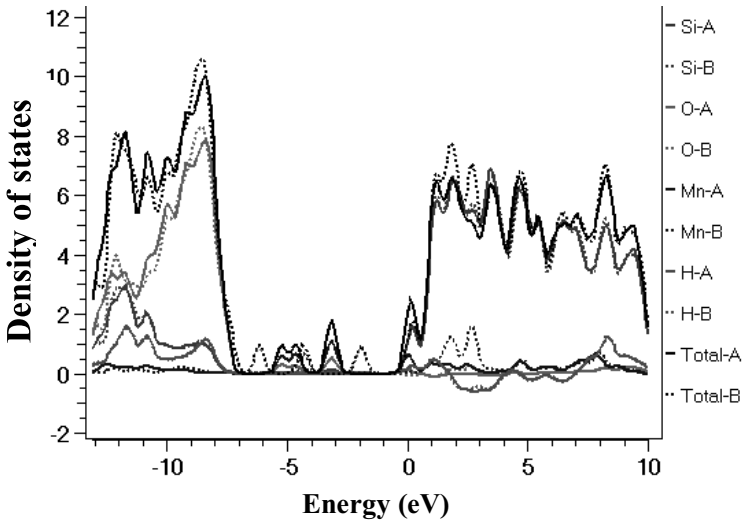


Figure 10. Plot of the density of states versus the energy of $Si_{17}MnO_{26}H_{32}$ structure using DFT method.