Calculation of Electronic Structures and Magnetic Properties of \(\alpha\)-quartz SiO\(_2\) with and without Transition Metal Elements

Pinit Kidkhunthod (พินิจ กิจขุนทด)
Tawan Remsungnen (เทวัญ เริ่มสูงเนิน)
Ekaphan Swatsitang (เอกพรรณ สวัสดิ์ซิตัง)

Abstract

Electronic structures and magnetic properties of pure \(\alpha\)-quartz SiO\(_2\) and doped \(\alpha\)-quartz Si\(_{1-x}\)M\(_x\)O\(_2\), 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 \(\alpha\)-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 \(\alpha\)-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 \(\alpha\)-quartz SiO\(_2\) than in pure \(\alpha\)-quartz SiO\(_2\), while the highest is found in Si\(_{17}\)MnO\(_{26}\)H\(_{32}\).

Keywords: Electronic structure, total dipole moment, \(\alpha\)-quartz SiO\(_2\);


corresponding author, e-mail: ekaphan@kku.ac.th

1Undergraduate Physics student, Department of Physics, Faculty of Science, Khon Kaen University, Thailand
2Lecturer, Department of Mathematics, Faculty of Science, Khon Kaen University, Thailand
3Assistant Professor, Integrated Nanotechnology Research Center, Department of Physics, Faculty of Science, Khon Kaen University, Thailand

Keywords: Electronic structure, total dipole moment, \(\alpha\)-quartz SiO\(_2\);

1Undergraduate Physics student, Department of Physics, Faculty of Science, Khon Kaen University, Thailand
2Lecturer, Department of Mathematics, Faculty of Science, Khon Kaen University, Thailand
3Assistant Professor, Integrated Nanotechnology Research Center, Department of Physics, Faculty of Science, Khon Kaen University, Thailand
4corresponding author, e-mail: ekaphan@kku.ac.th

Abstract

Electronic structures and magnetic properties of pure \(\alpha\)-quartz SiO\(_2\) and doped \(\alpha\)-quartz Si\(_{1-x}\)M\(_x\)O\(_2\), 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 \(\alpha\)-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 \(\alpha\)-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 \(\alpha\)-quartz SiO\(_2\) than in pure \(\alpha\)-quartz SiO\(_2\), while the highest is found in Si\(_{17}\)MnO\(_{26}\)H\(_{32}\).

Keywords: Electronic structure, total dipole moment, \(\alpha\)-quartz SiO\(_2\);

1Undergraduate Physics student, Department of Physics, Faculty of Science, Khon Kaen University, Thailand
2Lecturer, Department of Mathematics, Faculty of Science, Khon Kaen University, Thailand
3Assistant Professor, Integrated Nanotechnology Research Center, Department of Physics, Faculty of Science, Khon Kaen University, Thailand
4corresponding author, e-mail: ekaphan@kku.ac.th

Abstract

Electronic structures and magnetic properties of pure \(\alpha\)-quartz SiO\(_2\) and doped \(\alpha\)-quartz Si\(_{1-x}\)M\(_x\)O\(_2\), 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 \(\alpha\)-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 \(\alpha\)-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 \(\alpha\)-quartz SiO\(_2\) than in pure \(\alpha\)-quartz SiO\(_2\), while the highest is found in Si\(_{17}\)MnO\(_{26}\)H\(_{32}\).

Keywords: Electronic structure, total dipole moment, \(\alpha\)-quartz SiO\(_2\);

1Undergraduate Physics student, Department of Physics, Faculty of Science, Khon Kaen University, Thailand
2Lecturer, Department of Mathematics, Faculty of Science, Khon Kaen University, Thailand
3Assistant Professor, Integrated Nanotechnology Research Center, Department of Physics, Faculty of Science, Khon Kaen University, Thailand
4corresponding author, e-mail: ekaphan@kku.ac.th

Abstract

Electronic structures and magnetic properties of pure \(\alpha\)-quartz SiO\(_2\) and doped \(\alpha\)-quartz Si\(_{1-x}\)M\(_x\)O\(_2\), 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 \(\alpha\)-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 \(\alpha\)-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 \(\alpha\)-quartz SiO\(_2\) than in pure \(\alpha\)-quartz SiO\(_2\), while the highest is found in Si\(_{17}\)MnO\(_{26}\)H\(_{32}\).

Keywords: Electronic structure, total dipole moment, \(\alpha\)-quartz SiO\(_2\);

1Undergraduate Physics student, Department of Physics, Faculty of Science, Khon Kaen University, Thailand
2Lecturer, Department of Mathematics, Faculty of Science, Khon Kaen University, Thailand
3Assistant Professor, Integrated Nanotechnology Research Center, Department of Physics, Faculty of Science, Khon Kaen University, Thailand
4corresponding author, e-mail: ekaphan@kku.ac.th
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 $\alpha$-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 $\alpha$-quartz SiO$_2$ and doped $\alpha$-quartz SiO$_2$ with Mn, V and Cr have been calculated using Hartree Fock (HF) and Density Functional Theory (DFT) methods (Jensen, 1988).

Structure of $\alpha$-quartz SiO$_2$

The structure of $\alpha$-quartz SiO$_2$ is described by the space group P3$_2$1 and its hexagonal primitive vectors are: $\mathbf{A}_1 = \frac{1}{2} \mathbf{a}_x - \frac{1}{2} \sqrt{3} \mathbf{a}_y$, $\mathbf{A}_2 = \frac{1}{2} \mathbf{a}_x + \frac{1}{2} \sqrt{3} \mathbf{a}_y$, $\mathbf{A}_3 = c \mathbf{e}_z$.

Table 1 shows the coordinates of Si and O in $\alpha$-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 $\alpha$-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 $\alpha$-quartz and Si$_{17}$MO$_{26}$H$_{32}$ as doped $\alpha$-quartz in which M were V, Cr and Mn. The calculation yielded the density of states (DOS) and the total dipole moment of each $\alpha$-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 Hartree 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 $\alpha$-quartz SiO$_2$ and doped $\alpha$-quartz Si$_{1-x}$M$_x$O$_2$ 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 $\alpha$-quartz SiO$_2$ was reduced in comparison to pure $\alpha$-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 $\alpha$-quartz Si$_{1-x}$M$_x$O$_2$ are higher than those for pure $\alpha$-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 $\alpha$-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 $\alpha$-quartz SiO$_2$ and doped $\alpha$-quartz Si$_{1-x}$M$_x$O$_2$. The energy gaps of doped $\alpha$-quartz Si$_{1-x}$M$_x$O$_2$ 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 $\alpha$-quartz SiO$_2$ are higher than those of pure $\alpha$-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 $\alpha$-quartz SiO$_2$ doped with some transition metals such as Mn, V and Cr.

**Acknowledgements**

The Austrian–Thai Centre for Computer Assisted Chemical Education and Research, Chulalongkorn University and SMART LAB at the Department of Mathematics, Faculty of Science, Khon Kaen University are gratefully acknowledged.

**References**

Kidkhunthod, P. 2006. Calculation of Electronic Structures and Magnetic Properties of $\alpha$-quartz SiO$_2$ with and without Transition Metal Elements. Senior Project, Department of Physics, Faculty of Science, Khon Kaen University (in Thai).


Calculation of Electronic Structures and Magnetic Properties of \( \alpha \)-quartz \( \text{SiO}_2 \) with and without Transition Metal Elements

Table 1. The coordinates of Si and O in \( \alpha \)-quartz \( \text{SiO}_2 \) structure used in this study.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>-3.7590</td>
<td>-1.9995</td>
<td>-1.8017</td>
<td>O</td>
<td>-2.7567</td>
<td>-2.4931</td>
<td>2.4435</td>
</tr>
<tr>
<td>Si</td>
<td>-3.7590</td>
<td>1.9995</td>
<td>-3.6035</td>
<td>O</td>
<td>-3.8327</td>
<td>-3.1143</td>
<td>-0.6418</td>
</tr>
<tr>
<td>O</td>
<td>-3.2374</td>
<td>-0.6212</td>
<td>-1.1600</td>
<td>Si</td>
<td>1.1544</td>
<td>-1.9995</td>
<td>-1.8017</td>
</tr>
<tr>
<td>Si</td>
<td>-3.7590</td>
<td>1.9995</td>
<td>1.8017</td>
<td>Si</td>
<td>3.6111</td>
<td>2.2556</td>
<td>-1.8017</td>
</tr>
<tr>
<td>O</td>
<td>-3.2374</td>
<td>0.6212</td>
<td>1.1600</td>
<td>O</td>
<td>1.0807</td>
<td>3.1143</td>
<td>0.6418</td>
</tr>
<tr>
<td>Si</td>
<td>-0.7807</td>
<td>3.6339</td>
<td>-1.1600</td>
<td>Si</td>
<td>1.1544</td>
<td>1.9995</td>
<td>-3.6035</td>
</tr>
<tr>
<td>O</td>
<td>-3.8327</td>
<td>3.1143</td>
<td>0.6418</td>
<td>Si</td>
<td>-2.3088</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>O</td>
<td>-2.7567</td>
<td>2.4931</td>
<td>-2.4435</td>
<td>O</td>
<td>-0.3000</td>
<td>1.7620</td>
<td>2.4435</td>
</tr>
<tr>
<td>O</td>
<td>-2.7567</td>
<td>2.4931</td>
<td>2.9617</td>
<td>O</td>
<td>-1.3760</td>
<td>-1.1408</td>
<td>0.6418</td>
</tr>
<tr>
<td>Si</td>
<td>-1.3023</td>
<td>-2.2556</td>
<td>-3.6035</td>
<td>O</td>
<td>-1.3760</td>
<td>1.1408</td>
<td>-0.6418</td>
</tr>
<tr>
<td>O</td>
<td>-2.7567</td>
<td>-2.4931</td>
<td>-2.9617</td>
<td>O</td>
<td>-0.3000</td>
<td>-1.7620</td>
<td>-2.4435</td>
</tr>
<tr>
<td>Si</td>
<td>-1.3023</td>
<td>-2.2556</td>
<td>1.8017</td>
<td>O</td>
<td>1.6760</td>
<td>0.6212</td>
<td>1.1600</td>
</tr>
</tbody>
</table>

Table 2. The Energy gaps of pure and doped \( \alpha \)-quartz \( \text{SiO}_2 \) calculated by HF and DFT methods.

<table>
<thead>
<tr>
<th>Structure</th>
<th>( E_g ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>HF method</strong></td>
<td><strong>DFT method</strong></td>
</tr>
<tr>
<td>( \text{Si}<em>{18}\text{O}</em>{26}\text{H}_{32} )</td>
<td>15.766</td>
</tr>
<tr>
<td>( \text{Si}<em>{17}\text{VO}</em>{26}\text{H}_{32} )</td>
<td>4.359</td>
</tr>
<tr>
<td>( \text{Si}<em>{17}\text{CrO}</em>{26}\text{H}_{32} )</td>
<td>10.074</td>
</tr>
<tr>
<td>( \text{Si}<em>{17}\text{MnO}</em>{26}\text{H}_{32} )</td>
<td>10.062</td>
</tr>
</tbody>
</table>
Table 3. The values of total dipole moments of each SiO$_2$ structure calculated by HF and DFT methods.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Total dipole moment (Debye)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HF method</td>
</tr>
<tr>
<td>Si$<em>{18}$O$</em>{26}$H$_{32}$</td>
<td>4.0479</td>
</tr>
<tr>
<td>Si$<em>{17}$VO$</em>{26}$H$_{32}$</td>
<td>3.5726</td>
</tr>
<tr>
<td>Si$<em>{17}$CrO$</em>{26}$H$_{32}$</td>
<td>4.7830</td>
</tr>
<tr>
<td>Si$<em>{17}$MnO$</em>{26}$H$_{32}$</td>
<td>5.1349</td>
</tr>
</tbody>
</table>

Figure 1. The structures of Si$_{18}$O$_{26}$ (a) and Si$_{18}$O$_{26}$H$_{32}$ (b).
Calculation of Electronic Structures and Magnetic Properties of $\alpha$-quartz SiO$_2$ with and without Transition Metal Elements

Figure 2. Flowchart for the calculation of the density of states and the total dipole moment of pure and doped $\alpha$-quartz SiO$_2$ based on HF and DFT methods (Kidkhunthod, 2006).
Calculation of Electronic Structures and Magnetic Properties of \( \alpha \)-quartz SiO\(_2\) with and without Transition Metal Elements

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.
Calculation of Electronic Structures and Magnetic Properties of α-quartz SiO$_2$ with and without Transition Metal Elements

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.
Calculation of Electronic Structures and Magnetic Properties of $\alpha$-quartz SiO$_2$ with and without Transition Metal Elements

**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$_{28}$H$_{32}$ structure using DFT method.

Figure 10. Plot of the density of states versus the energy of Si$_{17}$MnO$_{28}$H$_{32}$ structure using DFT method.