Structural and Spin Polarization Effects of Cr, Fe and Ti Elements on Electronical Properties of \(\alpha\)-Al\(_2\)O\(_3\) by First Principle Calculations

Hossein Asghar Rahnamaye Alibad, Shaban Reza Ghorbani
Department of Physics, Sabzevar Tarbiat Moallem University, Sabzevar, Iran
E-mail: h.rahnama@sttu.ac.ir, h_rahnamay@yahoo.com
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Abstract

Structural and spin polarization effects of Cr, Fe and Ti elements on electronical properties of alumina have been studied by using of Local spin density approximation within density functional theory. The calculated results indicated that substituting aluminium atoms by these dopants have a significant influence on the structural and electronic properties of \(\alpha\)-Al\(_2\)O\(_3\) crystals. Band gap of alumina decreases with the substitution of these impurities. Results show that band gap is different for spin-up and down (spin splitting effect). Among these impurities the effect of Ti on size of the energy gap is small in comparison with Cr and Fe. It is suggested that the origin of electrons spin splitting is appeared from exchange energy of d-states. These results may be useful to obtain a physical behaviour of transition metals for electrons spin polarization in d-states.

Keywords: LSDA, Spin Polarization, Alumina, Transition Metals

1. Introduction

A unique combination of alumina with transition metals is very important due to their possible industrial applications. The corundum or sapphire phase of alumina (\(\alpha\)-Al\(_2\)O\(_3\)) has widespread applications in ceramic and semiconductor industry [1]. In order to improve electrical and optical properties of alumina, it can be doped by other metals; this requires the variation of electrical properties by theoretical calculations. Good substitutions on the Al atom sites are transition metals (TM), because the d-bands in these metals are partially filled and extended over the band gap. The substitutions of these metals change the band gap size and improve alumina properties.

Nearly all atoms have multiple electrons but most of them are paired up with another opposite spin electrons in the orbital. Solid magnetic properties are derived from the ground state properties of incompletely filled electron shells. Observed magnetic response, in a particular system largely depends on how the spin and orbital properties of these electrons end up in consideration of Pauli’s exclusion principle and minimizing Coulomb repulsion [2].

In this work, the influence of spin polarization Cr, Fe and Ti elements on electrical properties of alumina have been studied. Spin polarization is the first rule of Hound for determining the ground state (lowest energy) of electronic configuration in an atom. According to these rules and Pauli’s exclusion principle, electrons have been arranged in a way to have maximum total spin, S. In fact, these minimize Coulomb energy so that two parallel spins can not be in the same state. Energy decreasing due to the preference of being parallel spins is called exchange energy. In solids, depending on whether the crystal is insulating or conducting, magnetism has historically been approached from two different schools of thinking: either a localized or itinerant point of view. In the localized concept of magnetism, the electrons and their magnetic properties remain associated with their respective paramagnetic ion in an insulating crystal. Conversely, in the itinerant picture, the conduction electrons are responsible for magnetism. The magnetic of ordering may arise based on the specific alignment of the atomic magnetic moments, favoured by atomic exchange interactions and itinerant magnetism which is associated with metallic behaviour.

Normally, in a metal, there is an equal number of spin-up and spin-down electrons which fill up states to the Fermi energy. In the absence of an external field, a stable
ferromagnetic state can only arise if there is a spontaneous splitting of the spin population in the bands. This property is called spin polarization [2]. Pauli Hamiltonian in a magnetic system is

$$H_p = -\frac{\hbar^2}{2m} \nabla^2 + V_{ef} + \mu_s \sigma \cdot B_{ef} + \xi (\sigma \cdot l) + \cdots$$  \hspace{1cm} (1)$$

where the third and fourth terms refer to spin polarization and spin orbit interaction, respectively, so that in this work we have neglected from spin orbit interaction. $V_{ef}$ and $B_{ef}$ are electrostatic potential and effective magnetic field, respectively, and they are defined by the following Equations:

\begin{align*}
V_{ef} &= V_{ext} + V_H + V_{sc} \hspace{1cm} (2) \\
B_{ef} &= B_{ext} + B_{sc} \hspace{1cm} (3)
\end{align*}

where $V_H$ and $V_{sc}$ are Hartree and exchange-correlation potential, respectively. In the local Spin Density Approximation (LSDA), $V_H$ and $V_{sc}$ are defined as following:

\begin{align*}
V_{sc} &= \xi_{sc}(n,m) + \frac{\partial \xi_{sc}(n,m)}{\partial m} m \\
B_{sc} &= n \frac{\partial \xi_{sc}(n,m)}{\partial m} m
\end{align*}

where $\hat{m}$ and $n$ are magnetic dipole moment and spin density of electrons, respectively. In the spin space, due to Pauli spin operators, Pauli Hamiltonian is a $2 \times 2$ matrix and wave function is a two component vector (spinor):

$$H_p \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \xi \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} \hspace{1cm} (6)$$

where $\psi_1$ and $\psi_2$ are spin-up and spin-down components. For non magnetic compositions, spin-up density of electrons is equal with spin-down density of electrons. Therefore, total magnetic dipole moment of electrons is zero. Since in magnetic compositions, spin-up density of electrons is not equal with spin-down, the total magnetic dipole moment of electrons is not zero and spin splitting of electrons is occurred by exchange splitting, which is shown in Figure 1 [3].

2. Method of Calculations and Crystal Structure

In performance our calculations we have used the Full-Potential Linearized Augmented Plane Wave plus Local Orbital (FP-LAPW+LO) method. It is based on the density functional theory (DFT) as implemented in WIEN2K code [4]. The Local Spin Density Approximation (LSDA) is applied for the exchange-correlation interactions.

The LAPW+LO method for Cr, Fe and Ti elements is suitable because these impurities have localized d states. The structure of $\alpha$-Al$_2$O$_3$ is hcp that consists of close-packed planes of oxygen and aluminium. Its space group is R-3c with number 167. There are 12 Al atoms and 18 O atoms (30 atoms) in the unit cell of $\alpha$-Al$_2$O$_3$. The Cr, Fe and Ti atoms, which have the same valence with Al (+3), are substitute at octahedral sites within the alumina structure in the Al sites (Figure 2).

For calculation of lattice constants, lattice energy variation as a function of the deviation of $c/a$ (ratio, %) in constant volume have calculated from experimental values for $\alpha$-Al$_{2-x}$TxO$_3$ (T: Cr, Fe, Ti; $x = 0.5$). These results are shown in Table 1. It can be seen that our results good agreement with experimental results for $\alpha$-Al$_2$O$_3$. Then with calculated lattice constants, relaxed atomic positions were obtained for $\alpha$-Al$_2$O$_3$ and $\alpha$-Al$_{2-x}$TxO$_3$ (T: Cr, Fe, Ti; $x = 0.5$).

3. Results and Discussion

Alumina is a non-magnetic composition with high dielectric
Table 1. Calculated lattice constants for \(\alpha\)-Al\(_2\)O\(_3\) and \(\alpha\)-Al\(_{2-x}\)T\(_x\)O\(_3\) (T: Cr, Fe, Ti; x=0.5).

<table>
<thead>
<tr>
<th>Compositions</th>
<th>This work(Å)</th>
<th>Others(Exp., Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha)-Al(_2)O(_3)</td>
<td>a = b = 4.75699, c = 12.98769</td>
<td>a = b = 4.765 [5], c = 13.001</td>
</tr>
<tr>
<td>(\alpha)-Al(<em>{1.5})Cr(</em>{0.5})O(_3)</td>
<td>a = b = 4.75899, c = 12.97680</td>
<td>---</td>
</tr>
<tr>
<td>(\alpha)-Al(<em>{1.5})Fe(</em>{0.5})O(_3)</td>
<td>a = b = 4.75852, c = 12.97936</td>
<td>---</td>
</tr>
<tr>
<td>(\alpha)-Al(<em>{1.5})Ti(</em>{0.5})O(_3)</td>
<td>a = b = 4.76453, c = 12.94666</td>
<td>---</td>
</tr>
</tbody>
</table>

Figure 3. Considered symmetric direction in first brillouin zone for calculation of band structure of \(\alpha\)-Al\(_2\)O\(_3\) and \(\alpha\)-Al\(_{2-x}\)T\(_x\)O\(_3\) (T: Cr, Fe, Ti; x = 0.5).

Figure 4. Calculated density of states and band structure for \(\alpha\)-Al\(_2\)O\(_3\).

The calculated electronic band structure and density of states of \(\alpha\)-Al\(_{1.5}\)Cr\(_{0.5}\)O\(_3\), \(\alpha\)-Al\(_{1.5}\)Fe\(_{0.5}\)O\(_3\) and \(\alpha\)-Al\(_{1.5}\)Ti\(_{0.5}\)O\(_3\) are shown in Figures 5-7. By comparing Figure 4 and Figures 5-7, it can be seen that the substitution of Cr, Fe and Ti for Al in \(\alpha\)-Al\(_2\)O\(_3\) structure results in reducing the band gap. The band gap decreases mainly due to Cr, Fe and Ti-d state in the conduction band in different energies.

The obtained results from Figures 5-7, show that for all compositions, the energy gaps are smaller for spin-up states than spin-down. Therefore, electrical properties are different for both states and they can be applicable in spintronic devices. As can be seen in Table 3, among these impurities the effect of Ti on size of the energy gap is smaller in comparison with Cr and Fe. These are related to exchange energy splitting of d-states and magnetic properties of these materials.

4. Conclusions

The results of obtained show that the alumina energy gap was decreased by substitution of Cr, Fe and Ti impurities on the Al sites in \(\alpha\)-Al\(_2\)O\(_3\). It was found that energy gaps were different for spin-up and spin-down states for all \(\alpha\)-Al\(_{2-x}\)T\(_x\)O\(_3\) (T: Cr, Fe, Ti; x=0.5) compositions. Therefore, electrical properties are depended on spin polarization of electrons. Spin splitting effect were appeared from...
exchange interaction among the electrons in d-states. These results may be useful to obtain a physical picture of electrons spin polarization in d-states of transition metals. Among these impurities, the Cr element has the stronger spin splitting effect than the other impurities (Fe and Ti) in Alumina.

5. Acknowledgements

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6. References