Scientific
Research

Structural and Spin Polarization Effects of Cr, Fe and Ti Elements on Electronical Properties of α–Al₂O₃ 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*

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 α–Al₂O₃ 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 beheviour of transition metals for electrons spin polarization in d-states.

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 (α–Al₂O₃) 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

$$H_p = -\frac{\hbar^2}{2m}\nabla^2 + V_{ef} + \mu_B \boldsymbol{\sigma} \cdot \boldsymbol{B}_{ef} + \xi(\boldsymbol{\sigma} \cdot \boldsymbol{l}) + \cdots \quad (1)$$

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:

$$V_{ef} = V_{ext} + V_H + V_{xc} \quad (2)$$

$$B_{ef} = B_{ext} + B_{xc} \quad (3)$$

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

$$V_{xc} = \varepsilon_{xc}(n,\boldsymbol{m}) + n\frac{\partial \varepsilon_{xc}(n,\boldsymbol{m})}{\partial n} \quad (4)$$

$$\boldsymbol{B}_{xc} = n\frac{\partial \varepsilon_{xc}(n,\boldsymbol{m})}{\partial m}\hat{m} \quad (5)$$

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 2×2 matrix and wave function is a two component vector (spinor):

$$H_p\begin{pmatrix}\psi_1 \\ \psi_2\end{pmatrix} = \varepsilon\begin{pmatrix}\psi_1 \\ \psi_2\end{pmatrix} \quad (6)$$

where ψ_1 and ψ_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

Figure 1. Spin density of electrons for (a) non magnetic compositions (b) magnetic compositions.

suitable because these impurities have localized d states. The structure of α–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 α–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 α–Al$_{2-x}$T$_x$O$_3$ (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 α–Al$_2$O$_3$. Then with calculated lattice constants, relaxed atomic positions were obtained for α–Al$_2$O$_3$ and α–Al$_{2-x}$T$_x$O$_3$ (T: Cr, Fe, Ti; x = 0.5).

3. Results and Discussion

Alumina is a non-magnetic composition with high dielectric

Figure 2. The unit cell of α−Al$_{2-x}$T$_x$O$_3$ (T: Cr, Fe, Ti; x = 0.5) used in this study.

Table 1. Calculated lattice constants for α–Al_2O_3 and α-$Al_{2-x}T_xO_3$ (T: Cr, Fe, Ti; x=0.5).

Compositions	This work(Å)	Others(Exp., Å)
α—Al_2O_3	A = b = 4.75699 C = 12.98769	a = b = 4.765 [5] c = 13.001
α—$Al_{1.5}Cr_{0.5}O_3$	a = b = 4.75899 c = 12.97680	--- ---
α—$Al_{1.5}Fe_{0.5}O_3$	a = b = 4.75852 C = 12.97936	--- ---
α—$Al_{1.5}Ti_{0.5}O_3$	a = b = 4.76453 C = 12.94666	--- ---

constant. Symmetric direction for calculation of band structure in the first brillouin zone of α–Al_2O_3 and α–$Al_{2-x}T_xO_3$ (T: Cr, Fe, Ti; x = 0.5) is shown in **Figure 3**.

Energy zero was set at the top of valance band. Energy scale is in eV and the origin of energy was arbitrarily set to be at the maximum valance band. The calculated band structures and densities of states of α–Al_2O_3 are shown in **Figure 4**. Focusing on α–Al_2O_3, the bands with the widths 0 - 7 eV and 16-18.5 below the Fermi level are due to O 2p and 2s states. Al 3p and 3s states are appeared above the Fermi level in conduction band. The distance between the maximum of the conduction band and the minimum of the valence band (at the Γ point) will be denoted as band gap (E_g). There are a large number of localized states at the top of the valance band. These states are originating mainly from the O 2p atom. The valence band edges near the Fermi energy for O atom are quite sharp, while the conduction band edges near the Fermi energy are not. The valance band is composed of the O-2p orbital hybridized with the Al-3s, 3p and 3d orbitals. The lower valance is formed predominantly by O 2s atom. The contribution of Al 3d and Al 3p in the valance band are rather small.

A band gap of ~6.33 eV (without empirical correction factor) was obtained for α–Al_2O_3. That is fairly closed to experimental values. For comparison, the band gap results obtained from experimental measurements and other theoretical methods have been summarized in **Table 2**. It can be seen that our results agree qualitatively with experimental results. There is also a well agreement with the other theoretical calculations.
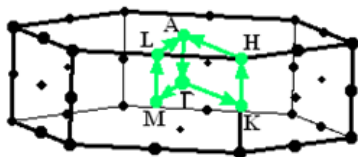
Figure 3. Considered symmetric direction in first brillouin zone for calculation of band structure of α–Al_2O_3 and α-$Al_{2-x}T_xO_3$ (T: Cr, Fe, Ti; x = 0.5).
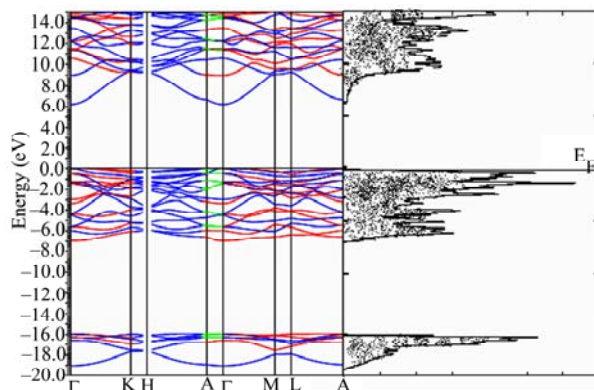
Figure 4. Calculated density of states and band structure for α–Al_2O_3.

Table 2. Obtained band gaps for Al_2O_3 by various methods.

Methods	Band gap (eV)
Experimental	
α—Al_2O_3 [6]	~10.8
α—Al_2O_3 [7]	~8.8
Amorphous alumina [8]	~8.7
Theory(LDA)	
κ—Al_2O_3 [9]	~5.3
α—Al_2O_3 [10]	~6.2
α—Al_2O_3 (this work)	~6.33

The calculated electronic band structure and density of states of α–$Al_{1.5}Cr_{0.5}O_3$, α–$Al_{1.5}Fe_{0.5}O_3$ and α–$Al_{1.5}Ti_{0.5}O_3$ 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 α–Al_2O_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 α–Al_2O_3. It was found that energy gaps were different for spin-up and spin-down states for all α–$Al_{2-x}T_xO_3$ (T: Cr, Fe, Ti; x=0.5) compositions. Therefore, electrical properties are depended on spin polarization of electrons. Spin splitting effect were appeared from
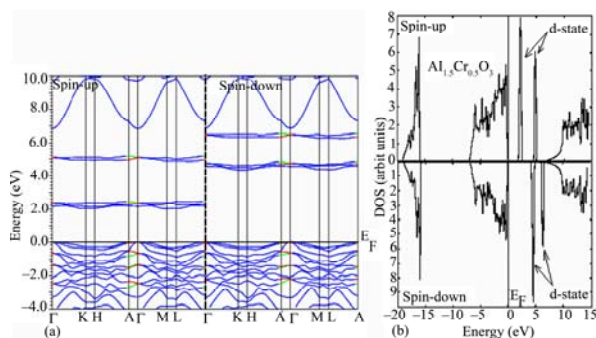
Figure 5. (a) Band structure of α-Al₁.₅Cr₀.₅O₃ (b) Density of states for α−Al₁.₅Cr₀.₅O₃.
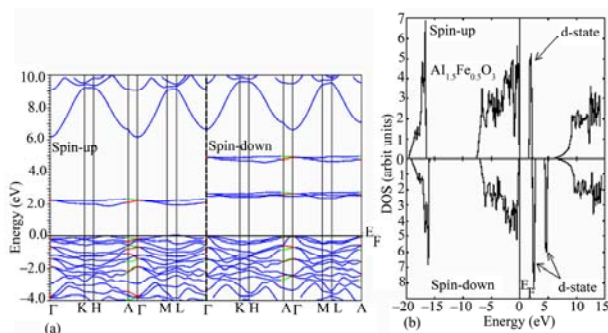
Figure 6. (a) Band structure of α−Al₁.₅Fe₀.₅O₃ (b) Density of states for α−Al₁.₅Fe₀.₅O₃.
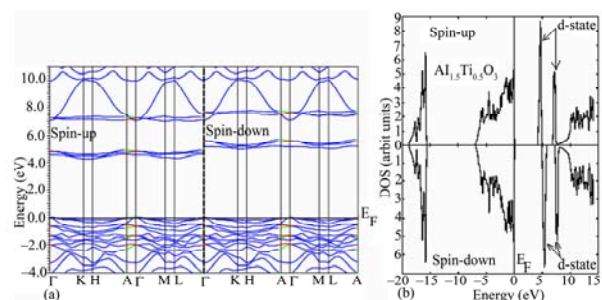
Figure 7. (a) Band structure of −Al₁.₅ Ti₀.₅O₃ (b) Density of states for α-Al₁.₅ Ti₀.₅O₃.

Table 3. Obtained band gap for α-Al₂O₃ and α-Al₂₋ₓTₓO₃ (T: Cr, Fe, Ti; x = 0.5) in spin-up and down states.

Compositions	Band gape (eV)	
	Spin-up	**Spin-down**
α−Al₂O₃	6.33	
α−Al₁.₅Cr₀.₅O₃	1.77	4.13
α−Al₁.₅Fe₀.₅O₃	1.56	2.04
α−Al₁.₅Ti₀.₅O₃	4.13	4.94

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

6. References

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