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First Principles Studies of the Effect of Nitrogen Impurities on the Energy Gap of Rutile $TiO_{2-x}N_x$ by Pseudopotential Approaches

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Abstract: We have studied the electrical properties of rutile $TiO_{2-x}N_x$ compound which x is the fraction of Ni impurities and was chosen to be 0.0625, 0.125, 0.25 and 0.5. In the calculations, we have adopted a pseudopotential and supercell approach based on the Density Functional Theory (DFT) with GGA approximation for the Exchange-correlation potential as implemented in SIESTA code. We have calculated the band structure and Density of State (DOS) and therefore, the changes of the energy gap of this compound with nitrogen substitution in oxygen sites. The quality of the used pseudopotential was tested by comparing the calculated band structure and DOS using Full Potential Linear Augmented Plane Wave (FP-LAPW) and pseudopotential methods. The result shows that the energy gap of $TiO_{2-x}N_x$ has decreases considerably due to the appearing of the N-2p orbitals in the bottom of the energy gap which is in good agreement with the recent experimental researches about the red shift of the threshold absorbance frequency of this compound which has made it an interesting photocatalysis in the visible spectrum of the solar radiation.

Key words: Density functional theory, pseudopotential, full potential linear augmented plane wave, titanium oxide, photocatalysis, Iran

INTRODUCTION

Recently TiO_2 has attracted a lot of interest in the scientific community due to its important and vital applications in industry. Because, it has very high attractive index it can be used as a pigment in painting, coating, ink, plastic and a lot of other things that use pigments (Whitehead, 1983).

One of the most important of its properties is its photocatalytic activity which first was observed by Fujishima and Honda (1972). Its photocatalytic activity can be employed for self cleaning and disinfecting under exposure to UV radiation (Mills *et al*., 1993). It also can be used to decompose NO_x in exhaust gases and environmental purification splitting of water for generating electric energy (Gratzel, 1983; Fujishima *et al*., 2000), killing bacteria by antibacterial activity of photocatalytic titanium dioxide (Wong *et al*., 2006).

Although, it has a lot of application but its photocatalytic activity is limited due to this fact that it works as a catalysis in UV radiation which firstly comprise a small fraction of radiation of solar spectrum and secondly will limit its application for outdoor using. One way for improving its photocatalytic activity and benefit from the visible light of solar radiation and therefore, indoor applications is doping it with other elements. Among the huge number of metal and non-metal elements, doping with nitrogen in a variety of routes has been widely reported by researchers in recent years (Zaleska, 2008; Nie *et al*., 2009; Bianchi *et al*., 2009; Liu *et al*., 2009). Nearly in most of this researches, it has been pointed out that the photo absorbance threshold energy of N-doped TiO_2 has been decreased with respect to pure samples which means that doping with nitrogen have caused a red shift in its absorbance region.

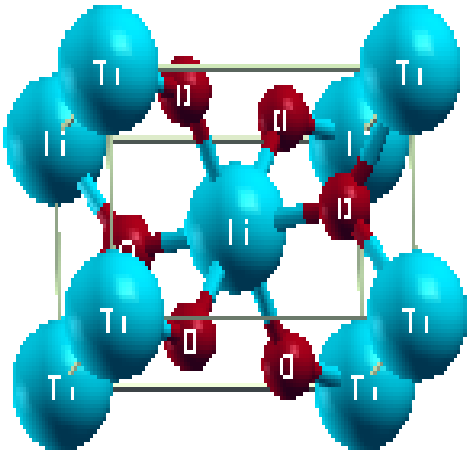

Fig. 1: The unit cell of rutile TiO_2

Titanium dioxide (TiO_2) crystallizes in several crystal structures which the most well-known of its crystals are: rutile (tetragonal), anatase (tetragonal) and brookite (rhombohedral) structures (Burdett *et al*., 1987).

Rutile structure which is the subject of this study is the most abundant and thermodynamically stable form of the 3 mentioned forms. It has tetragonal symmetry with P4/mnm space group (Wyckoff, 1948). The unit cell of rutile TiO_2 has been shown in Fig. 1. There are 6 atoms in its unit cell including 2Ti and 4O atoms. The purpose of this research is theoretical studying of the effect of nirtogen inurities on the band gap of rutile titanium dioxide by pseudopotential approaches which will be decribed in the study.

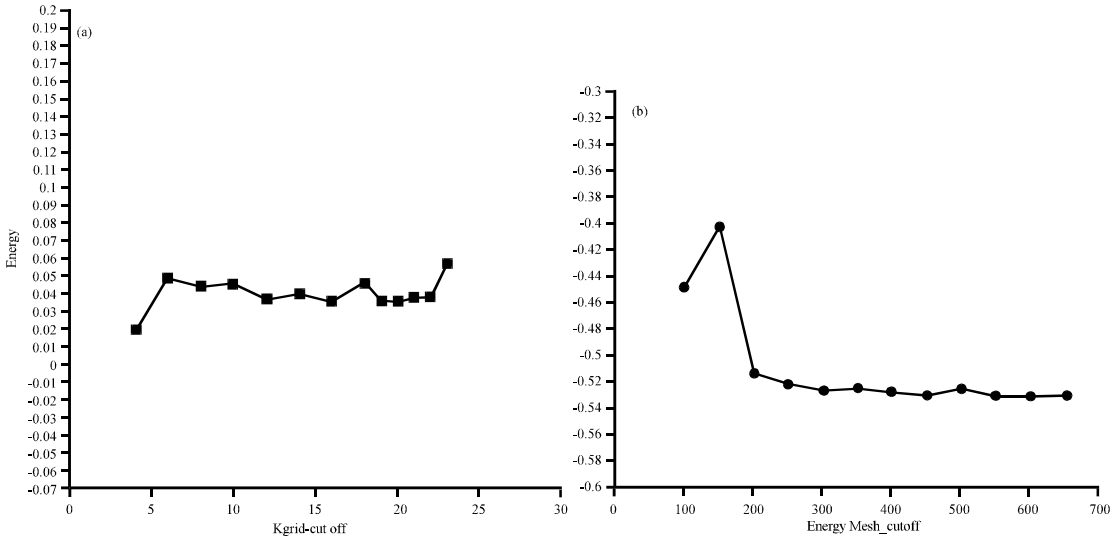

Fig. 2: Converging total energy with respect to (a) Kgrid_cut off and (b) Energy Mesh_cutoff

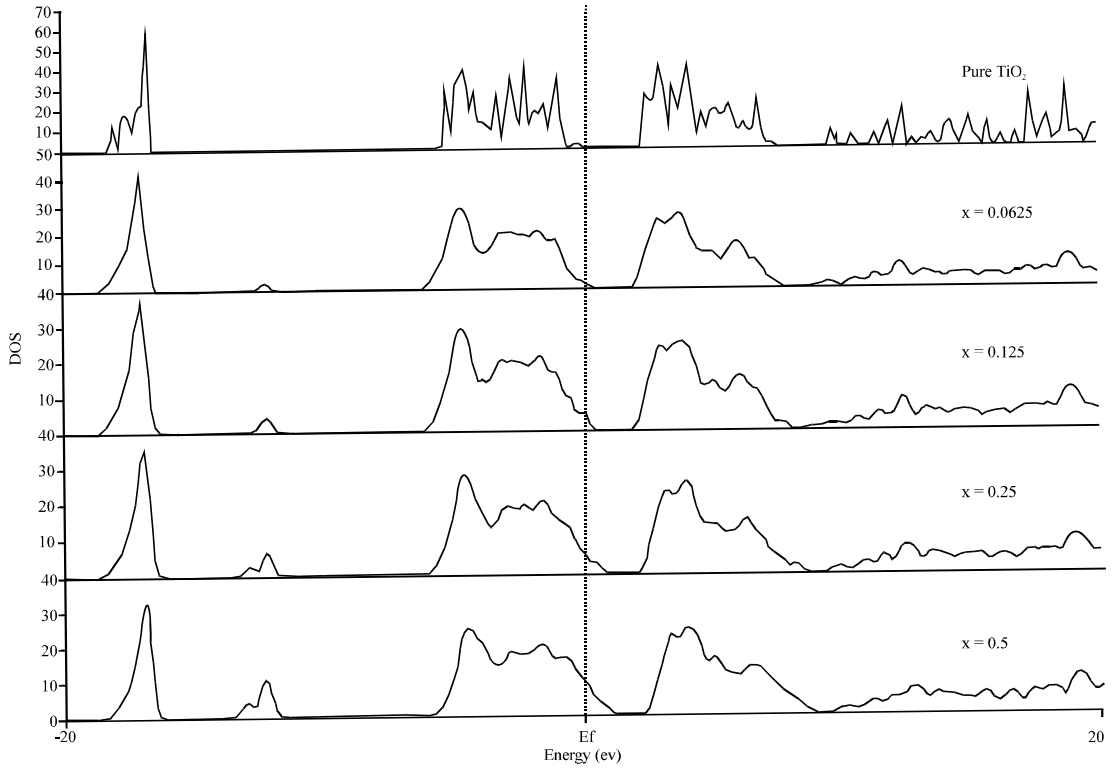

Fig. 3: Total density of state of pure and N-doped rutile $TiO_{2-x}N_x$

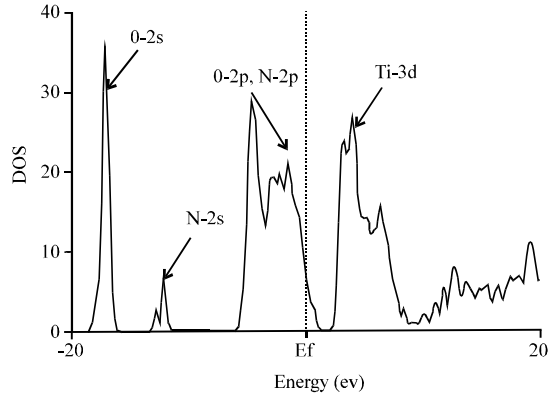

Fig. 4: Contribution of partial orbitals in total DOS of N-doped rutile $TiO_{2-x}N_x$

MATERIALS AND METHODS

In the calculation, we have used siesta code based on density-functional theory DFT within the local-density approximation LDA. Fully self-consistent Kohn-Sham functional was performed. Troullier-Martins pseudo-potentials were used to represent the nuclei plus core electrons. We made a 2×2×2 supercell of the unit cell which contain 48 atoms and then substituted some of the O atoms by N impurities. In this way, we made the nitrogen doped rutile $TiO_{2-x}N_x$ compound with x is the fraction of Ni and was chosen to be 0.0625, 0.125, 0.25, 0.5. There is two important parameter in SIEAT code which should be optimized correctly for saving time and also to have an acceptable precision in calculations. These parameters are Kgrid_cutoff and Mesh_cutoff energy where their optimized values were chosen from converging total energy to be 10A^0 and 300 Ry, respectively (Fig. 2).

RESULTS AND DISCUSSION

The calculated Density of State (DOS) of the pure and N-doped rutile $TiO_{2-x}N_x$ has been shown in Fig. 3. As it is obvious from the Fig. 3, doping with nitrogen has caused some energy levels emerge in the bottom of the energygap. These levels are belonging to the N-2p orbital of nitrogen impurities which is obvious from the calculated total DOS diagram of the N-doped rutile $TiO_{2-x}N_x$ (Fig. 4).

CONCLUSION

We see that with increasing the percent of substituted atoms, the threshold energy, i.e., the minimum energy which a photon should have inorder to produce one electron-hole pair in the valance and conduction band decreases with respect to pure samples. Therefore, doping titanium dioxide with Nitrogen will cause a shift in its absorbance spectrum from UV to the visible light region.

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