DENSITY FUNCTIONAL STUDY OF STRUCTURAL AND ELECTRONIC PROPERTIES OF Ca AND Mg DOPED TIO₂

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ABSTRACT
The scarcity of affordable and environment-friendly sources of energy has led to emergence of photo catalysis to mitigate this problem. This is so if the photo catalysts are active in solar energy spectrum. Environment-friendly, non-toxic and economical photo catalysts would find application in water treatment, providing another solution to the problem of clean water for domestic use. Of many materials available for photo catalysis is Titanium (IV) oxide (TiO_2). It possesses many merits such as low cost, high photocatalytic activity, non-toxicity and high availability. However, drawbacks that limit its application include its optical absorption that falls in the ultraviolet part of the electromagnetic spectrum. To extend the optical absorption to a wider region of the solar energy spectrum, various dopants have been added to the oxide to improve its solar efficiency. TiO_2 has rapid electron-hole recombination which leads to low rates of the desired chemical transformations in energy absorption. This research modified the structure and electronic properties of pure rutile TiO_2 by doping it with alkaline earth metals Ca and Mg for improved photocatalytic application. The objectives were structural optimization of rutile TiO_2 and alkaline metal (Mg, Ca) doped rutile using Density Functional Theory (DFT) and determination of electronic structure of rutile TiO_2 and alkaline metal (Mg, Ca) doped rutile using DFT. The DFT method as implemented in the Quantum ESPRESSO simulation package was used. The exchange correlation potential was treated with the Generalized Gradient Approximation. Total energy and ionic relaxation calculations were carried out after **k**-point and ECUT convergence tests. An ECUT energy of 40 Ry and 4x4x7 k-points were used for the total energy calculations. The optimized cell parameters for pure rutile crystal system are $a = b = 4.603\text{Å}$ $c = 2.992\text{Å}$. There is an expansion of the crystal structure and its volume slightly increased. The calculated band gap of undoped rutile is 1.8 eV, which reduces doping with Mg and Ca. There is a shift of the valence band edge to higher energies and introduction of intraband dopant states. The changes in electronic structure are favorable for absorbance of a wider spectrum of solar energy and reduction of charge recombination during photo catalysis. Alkaline earth metal doping of TiO_2 rutile modifies the structural and electronic properties of rutile TiO_2 in a manner that would make it a more efficient photo catalyst. Co-doping with the alkaline metal dopants could be attempted to investigate the combined effect.
Keywords: Band gap, Photo catalyst, Doping, Rutile TiO_2, Density functional theory, Generalized gradient approximation,

INTRODUCTION

Photo catalysis has emerged as one of the recent technologies for the mitigation against the scarcity, high prices and environmental pollution caused by fossil fuels in applications such as water treatment (Xiaolan *et al*., 2019). Provision of clean water to the society remains a number one priority for any government and society at large. This is due to the fact that the importance of clean water cannot be overstated, as it not only has a direct impact on the health of the population but is an absolute necessity for human existence. This has remained elusive, especially in Sub-Sahara countries in Africa. Problems arising to human beings and the environment from water contamination are currently on the increase. The majority of water problems have originated from industrial processes, with dye industries contributing highly to this challenging problem, as a result of the discharge of toxic chemicals as well as chemically stable organic dyes which resist natural degradation and some of which transform into carcinogenic agents (Ahmed *et al.,* 2016).

In the last three decades, Titanium (IV) Oxide (TiO_2) photo catalysis has been one of the most significant environmental remediation technology and an efficient technique for the treatment of contaminated drinking and industrial wastewaters (Fujishima & Zhang, 2005). The TiO_2 nanoparticle photo catalyst is widely used for the degradation and mineralization of many organic pollutants to harmless end products. Moreover, TiO_2 photo catalyst also plays a key role in the redox reactions of heavy metals to insoluble state, with the subsequent recovery and removal from the industrial effluents (Avasarala *et al.*, 2016). However, it suffers from a number of drawbacks that limit its application. First, its optical absorption falls in the ultraviolet part of the electromagnetic spectrum. To extend the optical absorption to a wider region of the solar energy spectrum, various dopants have been added to the oxide to improve its solar efficiency. TiO_2 has another major limitation of rapid electron-hole recombination which

leads to low rates of the desired chemical transformations with respect to absorbed energy. This study focuses on modification of the structure and electronic properties of pure rutile TiO_2 by doping it with alkaline earth metals Ca and Mg, for improved photocatalytic applications.

MATERIALS AND METHODS

Rutile has a tetragonal structure with space group 141/amd, having two titanium atoms and four oxygen atoms in the unit cell of reported experimental lattice parameters a = b = 4.57 Å, c = 2.95 Å.
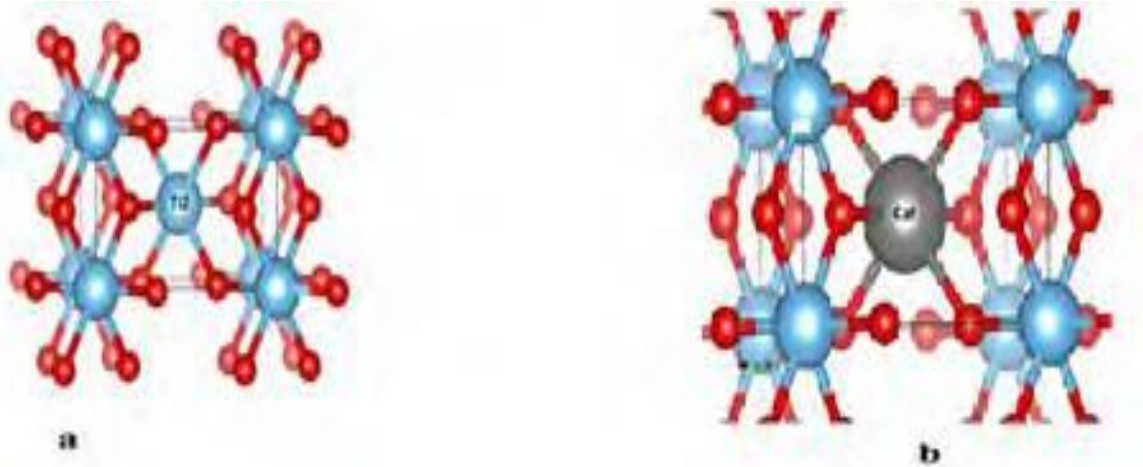The crystal structure for computational model is as shown in Figure 1.

Figure 1: a) Rutile unit cell b) Rutile with doped element at Ti site

Computational details

The Density Functional Theory (DFT) method as implemented by the Quantum ESPRESSO simulation package was used. The calculations to optimize the structure of rutile and to determine its electronic structure applied the generalized Gradient Approximation (GGA) to describe the exchange and correlation in the system. In this work the electron wave functions were in plane wave basis sets with the cut off energy of the wave function converged at 40Ry.The ionic levels were represented by Ultra Soft Pseudopotentials (USPP) for Ti, O, Ca and Mg atoms. For total energy and relaxation calculations, a 4 x 4 x 7 k point grid was chosen using the linear tetrahedron method with Blöchl correlations since it gives a smooth electron density of states. Electronic ground state energy was calculated through self-consistent cycles in combination with numerical methods such as David diagonalization schemes for evaluation of the solution to the Kohn Sham functional. Upon cation substitution, the structures were allowed to relax in order to minimize the forces in the system before total energy calculations were done. The maximum number of geometric and electronic iterations was set at 100.The iterations ended at a convergence criterion of 10^{-8} eV for most calculations. Generally, all calculations began from scratch.

RESULTS AND DISCUSSION

Structural Properties

The optimized cell parameters for pure rutile TiO_2 were $a = b = 4.603Å \; c = 2.992Å$, which are in good agreement with other theoretical values such as $a = b = 4.614 Å, c = 2.976 Å$ (Liu *et al.*, 2010). The calculated values from this work of cell parameters an and b by GGA are very close to experimental values, showing the reliability of the method.

To analyze geometrical changes after the dopant entering the lattice, the optimized cell parameters were calculated for the pure rutile TiO_2 and different doped models, as shown in Figure 2. In comparison to pure rutile TiO_2, the doped systems have larger lattice parameters, with the Ca-doped system being the largest. This is attributed to its larger ionic radius compared to Mg and Ti. On doping there is a slight expansion of the crystal structure and its volume slightly increases by 8.753 $(A^0)^3$ in doped Mg and by 28.816 $(A^0)^3$ in the Ca doped system.
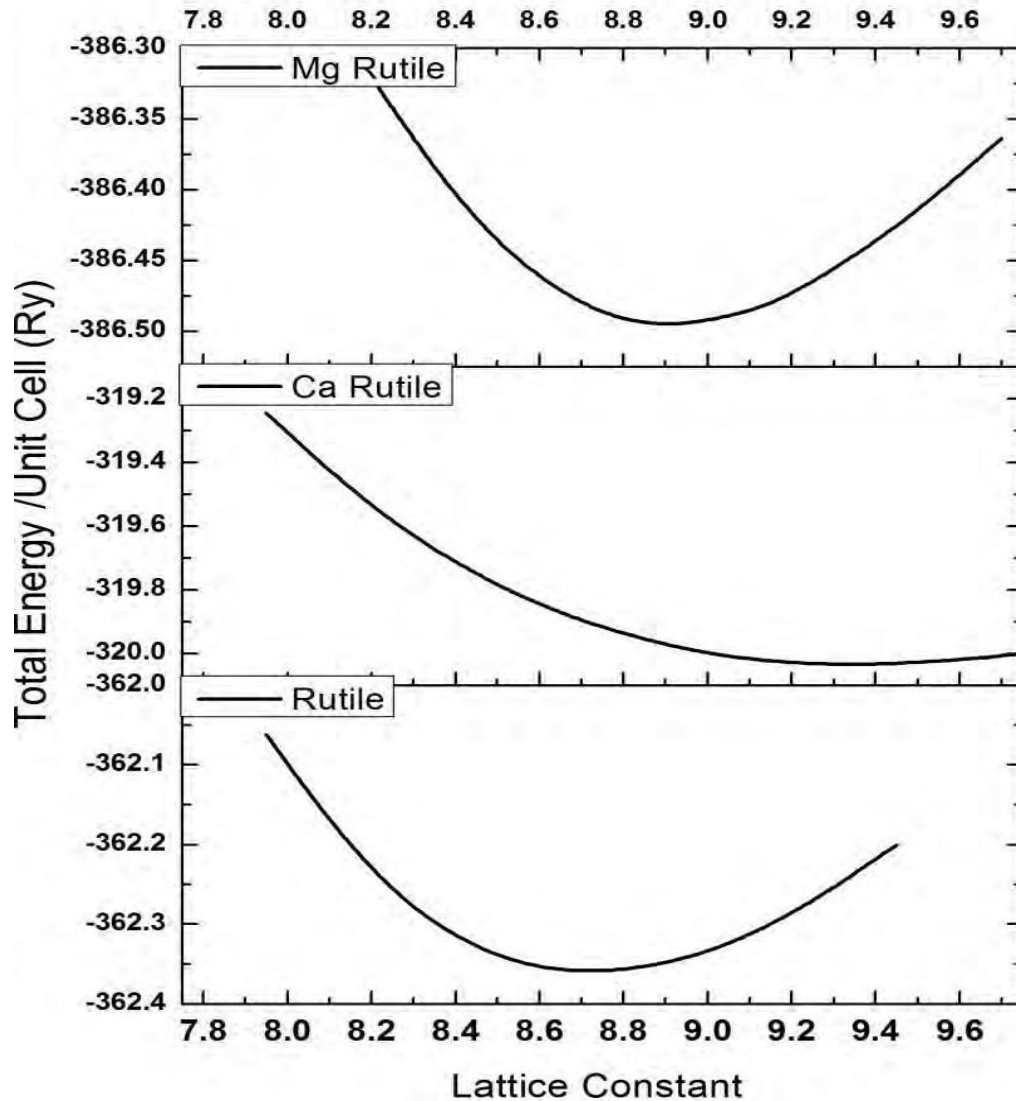
Figure 2: Total energy vs lattice constants of pure and doped Rutile

Table 1: The calculated cell parameters, crystal volume changes for the pure rutile TiO$_2$, Ca doped TiO$_2$ and Mg doped TiO$_2$.

Configuration	a (Å)	b(Å)	c(Å)	V(Å)^3	ΔV(Å)^3
Pure Rutile	4.603	4.603	2.992	63.393	-
Mg doped Rutile	4.736	4.736	3.221	72.246	8.753
Ca doped Rutile	4.974	4.974	3.73	92.209	28.816

ELECTRONIC PROPERTIES
Total Density of States (TDOS) and Projected Density of States (PDOS)
Figure 3 shows the TDOS and the PDOS for pure rutile TiO$_2$. The valence band of pure rutile is mainly composed of the O atom 2p orbitals, while the conduction band is mainly comprised of the Ti atom 3d orbital.
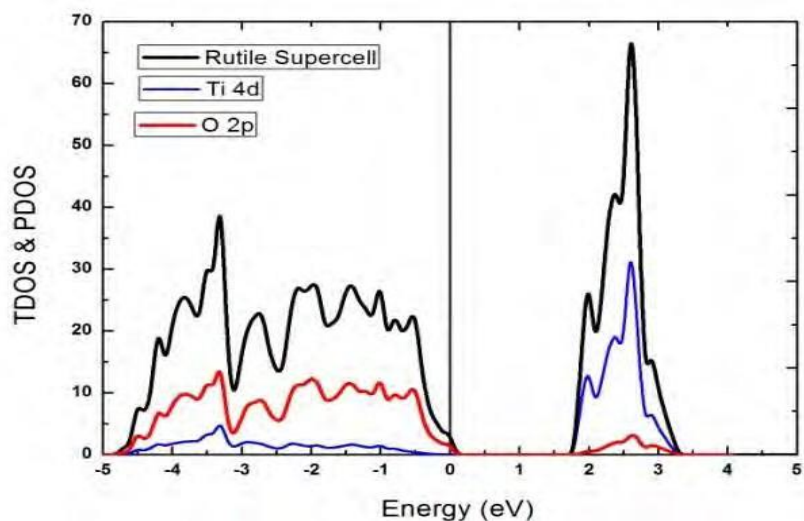
Figure 3: TDOS and PDOS of pure Rutile.

PDOS shows a shifting of the valence edge to higher energy in the doped systems. This is mainly due to the introduction of dopant states within the energy region as shown in Figure 4, which would contribute to hybridization with the *O 2p,* Ti 3*d* states of rutile.
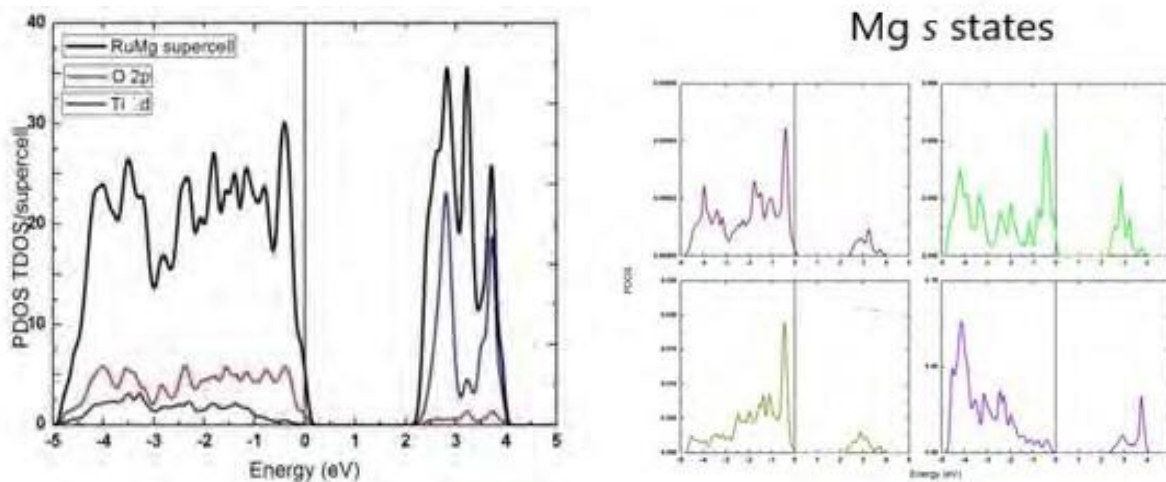

Figure 4: TDOS and PDOS Mg doped Rutile.

Similarly, Ca dopant states are found at the valence band edge, leading to the formation of interband states and a shifting of the valence band to higher energies as shown in Figure 5, an effect favorable for the enhancement of photo catalysis.

An investigation of the charge density difference reveals a change in the shape of distribution around the oxygen atoms for the different systems even at this very low dopant concentrations as shown in Figure 6.

Band structures
The pure rutile TiO_2 band structure is shown in Figure 7. The Fermi level has been chosen at zero-point energy, which is shown as dotted line in the figure.
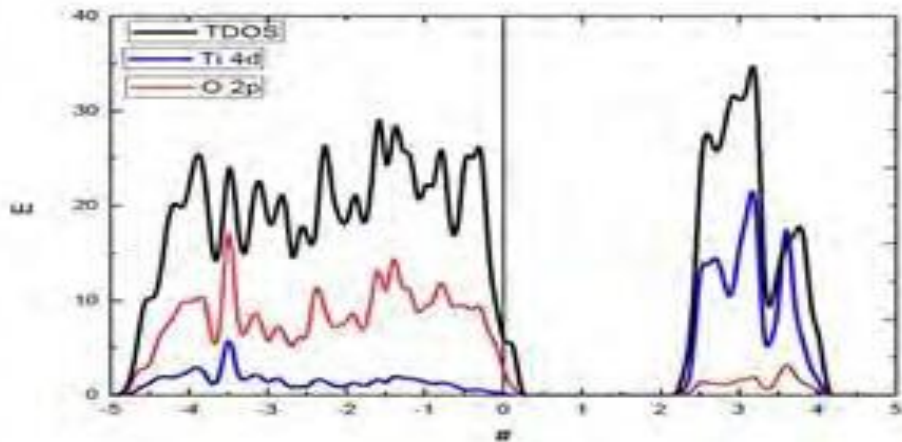
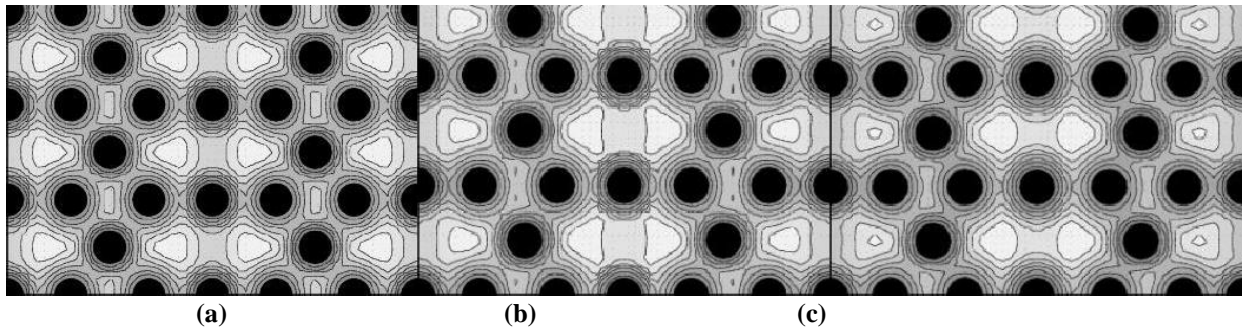**Figure 5: TDOS and PDOS of Ca doped Rutile.**

| (a) | (b) | (c) |

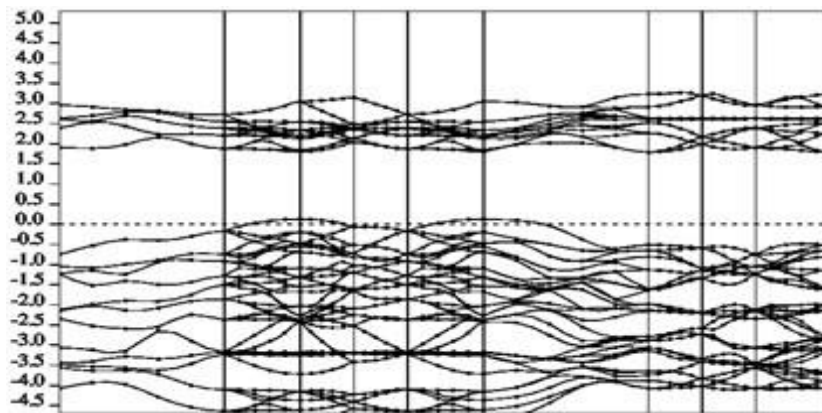**Figure 6: Charge density maps of (a) rutile, (b) Mg and (c) Ca doped rutile**

**Figure 7: Band structure of pure rutile.**

The calculated band gap of pure rutile is 1.8 eV which agrees well with the band gap from other theoretical calculations such as 1.86 eV calculated by Jin Feng *et al.*, 2014 as well as results from other studies as collated in Table 2.

Table 2: Rutile band gap and other theoretical and experimental results.

Rutile TiO$_2$	Band gap (eV)
This work	1.8
Other theoretical results	1.86 (Jin feng *et al.*,2014) 1.87 (Chen *et al.*,2017) 1.9 (Lindan *et al.*, 1997) 1.78 (Shang & Ching, 1995) 2.1 (Guo *et al.*, 2011) 2.048 (Zeng *et al.*, 2010)
Experimental results	3.0 (Pascual *et al.*, 1978) 3.0 (Landmann *et al.*, 2012) 3.0 (Reyes *et al.*, 2008)

These values are however less than the experimental value of 3.0 eV. This is expected since DFT underestimates the band gaps of insulators and semiconductors, but provides the necessary qualitative understanding of the effect of defects introduced on the trend in the change of the band gap upon introduction of defects.

Table 2 is a comparison of the findings with previous, corresponding theoretical and experimental ones. Ca and Mg dopant generates dopant states in the band gap, near the top of valence bands hence shifting valence bands to higher energy region, with a corresponding reduction in the band gap, even at this very low doping concentrations. The states are about 0.2 eV above the Fermi level for both Mg doped and Ca doped rutile as shown in Figure 8.
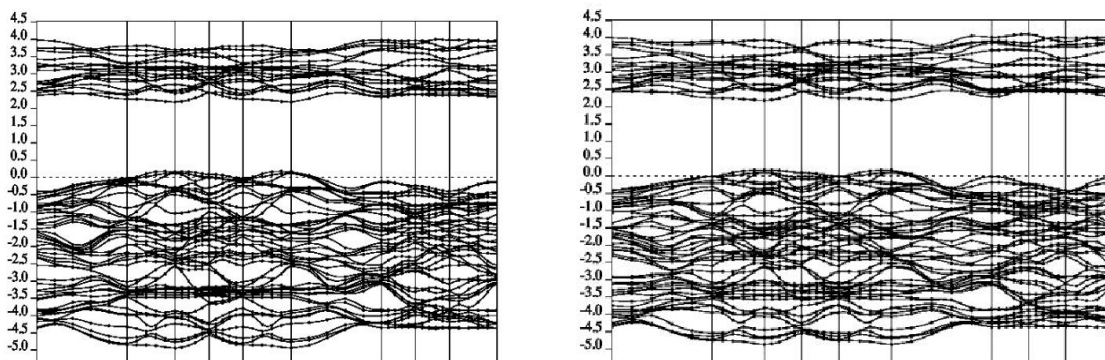
Figure 8: Band structure for Mg and Ca doped Rutile

CONCLUSION

There is a shift of the valence band edge towards higher energies and introduction of intraband dopant states with a corresponding reduction in the band gap. The observed changes in the electronic structure are favorable for the absorbance of a wider spectrum of solar energy and reduction of charge recombination during photo catalysis. Alkaline earth metal doping of TiO$_2$ rutile modifies the structural and electronic properties of rutile TiO$_2$ in a manner that would make it a more efficient photo catalyst

RECOMMENDATIONS

Co-doping with the alkaline metal dopants could be attempted to investigate the combined effect.

ACKNOWLEDGEMENT

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