DENSITY FUNCTIONAL STUDY OF STRUCTURAL AND ELECTRONIC PROPERTIES OF Ca AND Mg DOPED TiO_2

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ABSTRACT
The scarcity of affordable and environment-friendly sources of energy has led to emergence of photocatalysis to mitigate this problem. This is especially so if the photo catalysts are active in as much a wide region of the solar energy spectrum as possible. Environment-friendly, non-toxic and economical photocatalysts would find application in water treatment, providing another solution to the problem of clean water for domestic use. Of many materials available for photocatalysis 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 and rapid electron-hole recombination, which limits its photoquantum efficiency. To extend the optical absorption to a wider region of the solar energy spectrum, various dopants have been added to the oxide. In this study, the effect of doping rutile TiO_2 with alkaline earth metals Ca and Mg is investigated using the Density Functional Theory (DFT) method as implemented in the Quantum ESPRESSO simulation package, treating the exchange correlation potential with the Generalised Gradient Approximation. The optimized cell parameters for pure rutile crystal system are $a = b = 4.603$Å $c = 2.992$Å, with a volume of 63.393 $(Å)^3$. On doping there is a slight expansion of the crystal structure and its volume slightly increases by 8.753 $(Å)^3$ and 28.816 $(Å)^3$ with Mg and Ca doping respectively. The calculated band gap of undoped rutile is 1.8 eV. Mg and Ca doping raises the valence band edge by 0.2 eV in both Ca and Mg doped rutile. Dopant inter band and intra band states are observed that would be useful in mitigating against charge recombination hence enhancing the efficiency of the photocatalysts. Isolated O *2p* states are observed in the Projected Density of States (PDOS) of the doped systems which are normally attributed to enhanced optical absorption of photocatalysts in the visible region. 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 photocatalyst. Co-doping with the alkaline metal dopants could be attempted to investigate the combined effect.
Keywords: Rutile TiO_2, Density functional theory, Generalised gradient approximation, Doping, Band gap, Photocatalyst

INTRODUCTION
Photocatalysis 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 (Kang et al., 2019). Photodegradation using metal oxide photocatalysts is an efficient method for organic pollutant degradation and has proved to be an outstanding tool for degrading both aquatic and atmospheric organic pollutants. It uses the solar energy in the presence of a semiconductor photocatalyst to reduce the damage caused by environmental pollutants and wastewater treatment. Different semiconducting materials such as ZnO, CdS, ZnS, SnO_2, WO_3, Fe_2O_3 and Nb_2O_4 are abundantly available for photocatalysis, but only few of them are suitable for photo mineralization of a wide range of organic contaminants (Ahmed et al., 2013).

In the last three decades, Titanium (IV) Oxide (TiO_2) photocatalysis has been one of the most promising environmental remediation technologies and an efficient technique for the treatment of contaminated drinking and industrial wastewaters (Fujishima and Zhang, 2005; Tigabu *et al.*, 2021). The TiO_2 nanoparticle photocatalyst is capable of degradation and mineralization of many organic pollutants to harmless end products (Gaya and Abdullah, 2008). Moreover, TiO_2 photocatalyst also plays a key role in the redox reactions of heavy metals to insoluble state, with the subsequent recovery and removal from model 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 (Pesci *et al.*, 2013).

Various experimental and theoretical techniques such as metal and non-metal doping of TiO_2 have been undertaken in previous studies to make it more

technologically relevant and energy efficient (Graciani *et al.*, 2008). The use of non-toxic and readily available dopants to improve the application efficiency of TiO_2 has been a subject of both past and current research due to the wide applicability of the resulting materials in key areas such as water treatment and environmental remediation. Alkaline earth metal modified TiO_2 has been reported to demonstrate more efficient charge carrier separation from experimental approaches (Venkatachalam et al., 2007; Li et al., 2007; Zhang et al., 2014; Lv et al. 2019; Rhatigan et al., 2020). Mg doped TiO_2 has recently been reported to have improved degradation efficiency in both model industrial dyes (65–95%) and textile wastewater (92%) under natural sunlight (Shivaraju et al., 2017).

The experimentally synthesized TiO_2 has been found to have a mixed phase composition, comprising mainly of the anatase and rutile phases. While the anatase phase has been found to be the more photoactive phase, the rutile phase has been found to be most thermodynamically stable (Kim et al., 2021). More recently, theoretical approaches are proving complementary to the experimental efforts aimed at understanding and guiding the development of more efficient photocatalysts. The anatase phase of TiO_2 in particular has been reported to cause a shift in absorption to longer wavelengths and improved optical absorbance in visible and near-IR region upon doping with alkaline earth metals and transition metal dopants(Ma et al., 2015; Wang et al., 2014). Due to the mixed phase composition of TiO_2, a clear understanding on how each phase responds to modifications such as doping is pertinent in the development of more efficient photocatalysts. The anatase phase has dominated most of the theoretical investigations. 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 TiO_2 has a tetragonal structure with space group 141/amd, having two titanium atoms and four oxygen atoms in the unit cell and experimental lattice parameters a = b = 4.57 Å and c = 2.95 Å. The crystal structure for computational model is as shown in Figure 1.

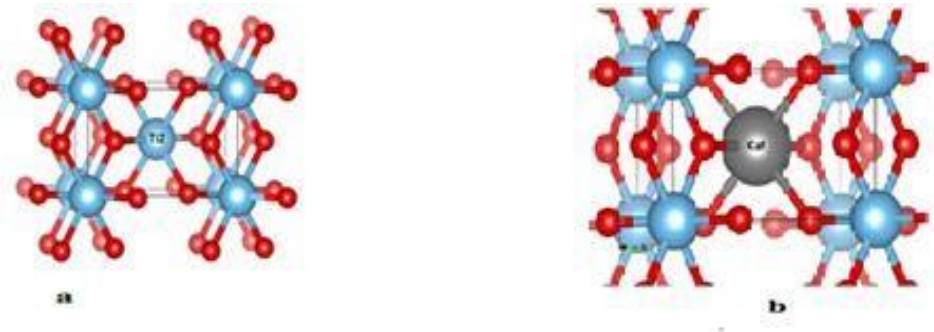


Figure 1: a) Rutile unit cell b) Rutile with doped element at Ti site

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 Generalised 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 Ultrasoft 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 corrections 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 equation. 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 are $a = b = 4.603Å$ $c = 2.992Å$, which are in good agreement with other theoretical values such as $a = b = 4.614$ Å, $c = 2.976$ Å (Liu et al., 2010) and others in Table 1. The cell parameters calculated from this work using 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 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 $(Å)^3$ and 28.816 $(Å)^3$in Mg and Ca doped systems respectively.

Table 1: Cell parameters and crystal volume changes for the pure and doped rutile TiO_2

Configuration	a (Å)	b(Å)	c(Å)	$V(Å)^3$	$\Delta V(Å)^3$
Pure Rutile	4.603	4.603	2.992	63.393	-
Other theoretical results	4.602[1]	4.602[1]	2.977[1]		
	4.630[2]	4.630[2]	2.980[2]		
	4.593[3]	4.593[3]	2.940[3]		
	4.623[4] 4.459[5]	4.623[4]	2.987[4]		
	4.690[6]	4.459[5]	2.902[5]		
	4.594[7]	4.690[6]	2.990[6]		
		4.594[7]	2.959[7]		
Experimental results	4.587[1] 4.593[2]	4.587[1]	2.955[1]		
		4.593[2]	2.959[2]		
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

[1] (Rubio-Ponce et al., 2008)[2](Burdett et al., 1987) [3](Chen et al., 2018) [4](Muscat et al., 1999) [5](Liu et al., 2009) [6](Lindan et al., 1997) [7](Zeng, 2015)

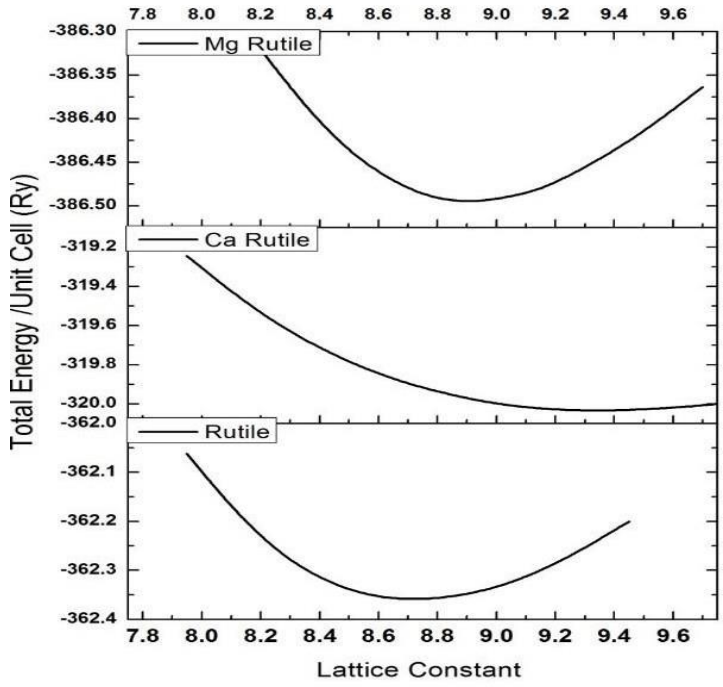


Figure 2: Total energy vs lattice constants of pure and doped rutile

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 *p* orbitals, while the conduction band is mainly comprised of the Ti *d* orbital. PDOS shows a shifting of the valence band 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 contributes to hybridization with the *O 2p*, Ti 3*d* states of 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 photocatalysis.

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

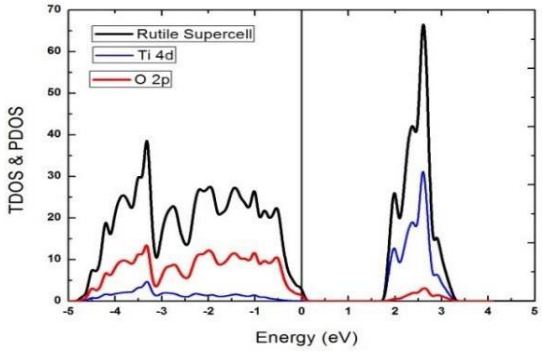


Figure 3: TDOS and PDOS of pure Rutile

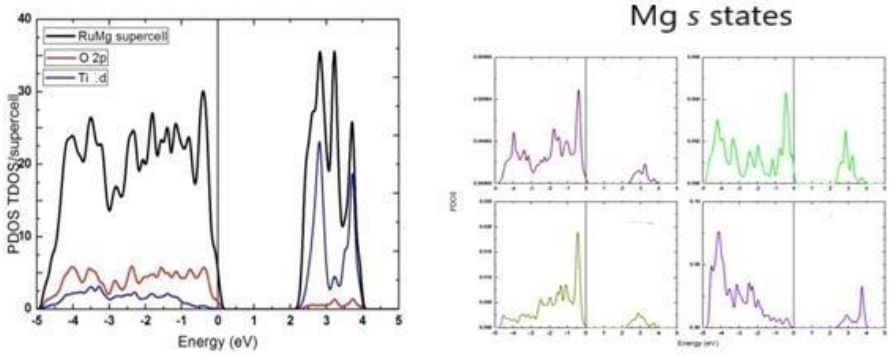


Figure 4: TDOS and PDOS Mg doped Rutile

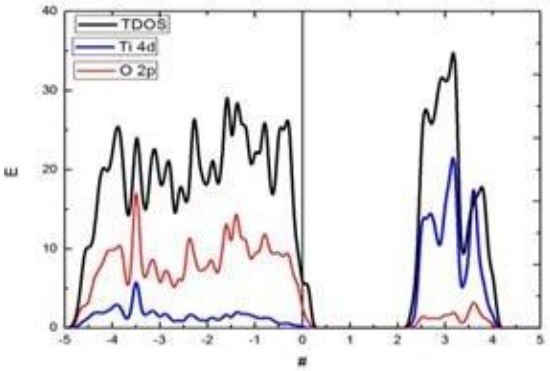
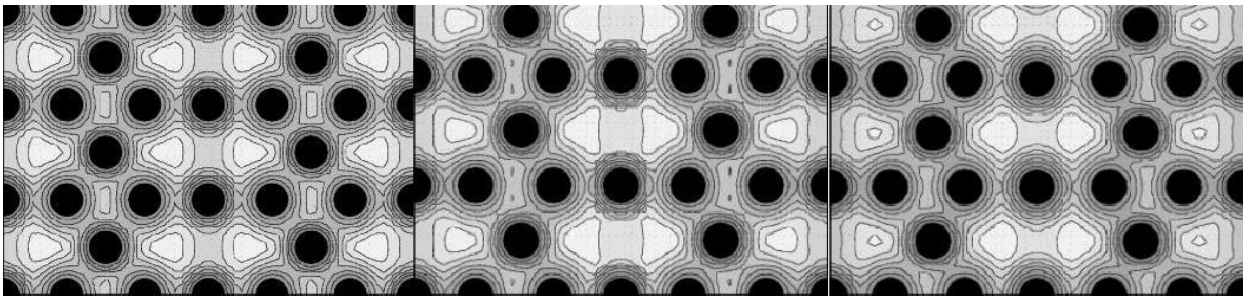


Figure 5: TDOS and PDOS of Ca doped Rutile



(a) (b) (c)

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

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 the dotted line in the figure. 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. Table 2 is a comparison of the findings with previous theoretical and experimental studies.

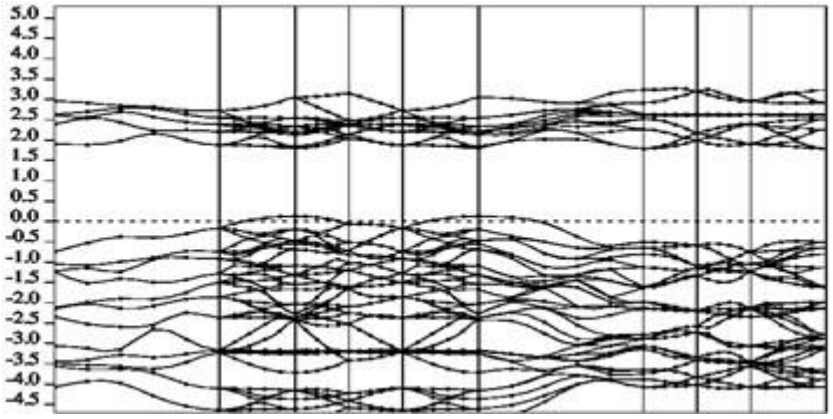


Figure 7: Band structure of pure rutile.

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

Rutile TiO_2	Band gap (eV)
This work	1.80
Other theoretical results	1.86 (Jin feng et al.,2014)
	1.87 (Chen et al.,2017)
	1.90 (Lindan et al., 1997)
	1.78 (Shang and Ching, 1995)
	2.10(Guo et al., 2011)
	2.05 (Zeng et al., 2015)
Experimental results	3.00 (Pascual et al., 1978)
	3.00 (Landmann et al., 2012)
	3.00 (Reyes et al., 2008)

The calculated 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.

Ca and Mg dopants generate 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.

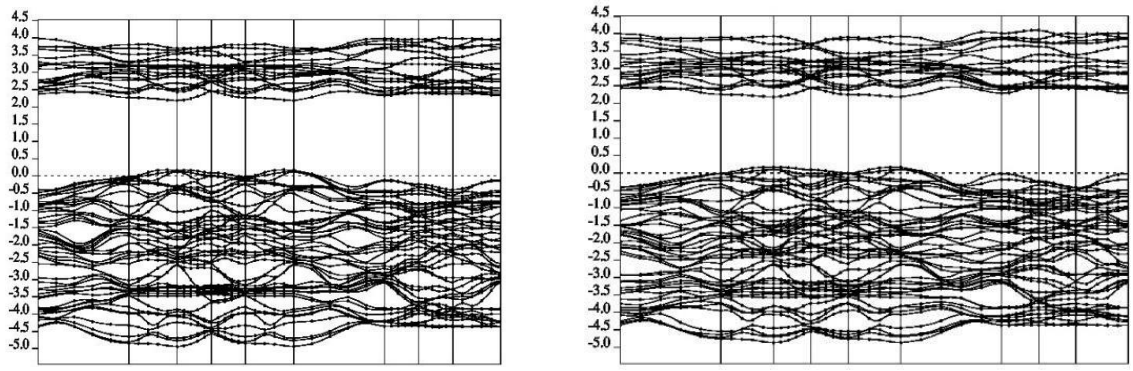


Figure 8: Band structure for Mg and Ca doped Rutile

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 photocatalysis. 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 photocatalyst

RECOMMENDATIONS

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

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