Ortho-atomic projector assisted DFT+U study of room temperature Ferro- and antiferromagnetic Mn-doped TiO2 diluted magnetic semiconductor

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Abstract

Using ortho-atomic Hubbard-corrected density functional theory, we present magnetic properties, ferromagnetic transition temperature Tc, Neel temperature TN, electronic structure, structural formation energy, and crystal structure of anatase (Ti16−xMnxO32 for x = 1, 2, 3, 4 and 6). According to the calculated formation energy, an oxygen-rich condition is more structurally stable than a Ti-rich situation. The geometric and lattice parameter optimization result indicates that Mn2+ exists in the system. In addition, when Mn is substituted in the system, some of the bonds that connect oxygen with the Mn ion are broken, and the bond lengths show variation; this results in defects, which cause the formation of oxygen vacancies that enhance both ferromagnetic and antiferromagnetic properties of the system. According to the structure of electronic bands and PDOS analysis, 2p and 3d hybridization lead to a decrease in the edge of the CB and an increase in the edge of the VB, narrowing the bandgap from 3.23 eV to 2.21 eV (for 4.17% of Mn), 2.13 eV (for 8.33% of Mn) and 1.69 eV (for 12.5% of Mn). Results also showed that both ferromagnetic and antiferromagnetic properties are energetically favored. Furthermore, the material exhibits antiferromagnetic with predicted TN to be 804.13 K for a small concentration of Mn dopant (for 4.17% of Mn), which is higher than room temperature. In contrast, the calculated ferromagnetic temperature (Tc) was increased from 255.42 K (for 8.33% of Mn) to 385.63 K (for 12.5% of Mn), most likely as a cause of bound magnetic polarons (BMPs) production. Result also reveals oxygen vacancy for the relaxed pristine (Ti16O31) a non-zero magnetic moment and a total magnetization of 2.00 μB which is observed as a result of an ortho-atomic projector. The present findings suggest that TiO2 could be tailored through doping and oxygen vacancy for versatile spintronic applications, inconsistent with previous experimental results.

1. Introduction

Dilute magnetic semiconductors (DMS) have obtained much focus due to their joint magnetic and transport properties, which are ideal for spintronic applications. Spin transistors, non-volatile memories, logic devices, and so on are examples of such devices. The Diluted magnetic semiconductors of transition metal (TM)-doped oxides have drawn a lot of attention recently because they are thought to be the best prospects for spintronic materials. As a semiconductor(SC) with a wide bandgap, TiO2 is interesting for photonic, electronic, and magnetic applications [1–4].

The spin of electrons was overlooked in conventional charge-based electronics until recently. However, after the concept of spintronics was introduced, information processing was understood to be carried out by electron spin rather than electron charge. This paved the way for a new class of devices that integrate conventional spin-dependent microelectronics caused by the interaction of the carrier’s spin with the magnetic characteristics of the material. In comparison to current semiconductors, these new devices would have less volatility, faster data processing, lower electrical power consumption, and higher integration densities [5].
It is widely assumed that ferromagnetism (FM) and antiferromagnetism (AFM) in semiconductors are mediated by a small proportion of transition metal (TM) dopants with a partially filled d or f shell. Certain dilute magnetic semiconductor materials on the basis of III-V and II-VI SCs, on the other hand, appear to possess intrinsic (carrier-induced) FM. [6]

Doping with a small amount of TM can also produce stable room temperature ferromagnetism (RTFM) in oxide semiconductors/insulators [7]. Following Dietl et al’s theoretical prediction for the ferromagnetism at room temperature in ZnO with Mn added [8], not only the ZnO doped with TM [9, 10] but also other oxide-based SCs doped with TM like SnO2 [11], TiO2 [12, 13], and HfO2 [14] were investigated experimentally as well as theoretically in a variety of morphologies for the RTFM.

Introducing magnetic impurities into such semiconducting oxides has generated a lot of interest in recent years as a result of its uncommon ability to mix existing semiconducting behavior with substantial magnetism [5, 15] and is referred to as dilute magnetic oxide semiconductors (DMOS). TiO2 is a notable and commonly utilized semiconductor with rutile and anatase structures and a large bandgap that is well altered through doping, for versatile optical, electronic, and magnetic properties [16].

A lot of work has been done, both experimental and theoretical, as discussed below. For example, experimentally as reported in [4], high Tc = 400 K ferromagnetism in Co-doped TiO2 synthesized via molecular beam epitaxy (MBE) using combinatorial pulsed-laser deposition (PLD) with a measured magnetic moment of 0.32μB/Co for Co concentrations up to 8% was observed. In another report, Ogale et al. [17] studied FM at room temperature in Co-doped rutile TiO2 using pulsed laser deposition (PLD). When Co is doped in rutile TiO2 at varying concentrations (x = 0–0.06), a layer grows at low temperatures in various reducing environments. The study shows a scenario involving multiple states of FM with dilute magnetic semiconductors and magnetism in a coupled cluster with cobalt affinities within the matrix at higher concentrations.

Fukumura et al. [18] used laser r-sapphire substrates and molecular beam epitaxy to prepare a Co-introduced rutile TiO2 (Ti1−xCoO2−x) epitaxial thin film. Their findings demonstrate that the charge imbalance and lattice distortion are caused by enormously generated oxygen vacancies and the Co2+ ion with high spin, which supports FM at high temperatures.

Rodriguez et al. [19] used a microemulsion approach to create nanoparticles of Fe doped TiO2 anatase phase, and an x-ray absorption technique to demonstrate the existence of Fe3+ at Ti4+ site in the doped TiO2, resulting in the formation of oxygen vacancies to maintain neutralization of charges. Using Motsub and magnetic measurements, they found electronic defects such as oxygen vacancies and magnetic dopant change ferromagnetism. However, there have been disagreements about the source of magnetism in DMOS. The observed magnetism is thought to be caused by either carrier-mediated magnetic ions [20] or external factors such as second phase development or clusters of magnetic impurity atoms. For instance, the bound magnetic polarons (BMPs) model was introduced by Coey et al. [21], suggesting that defect-related magnetic impurities as the principal source of observable magnetization in these systems. Besides, Choudhary et al. [22] investigated the influence of Mn on TiO2 nanoparticles generated by the sol-gel technique with sizes ranging from 6 to 11nm that exhibited magnetic properties at room temperature. Kim et al. [23] discovered oxygen vacancies in Mn-doped rutile TiO2 films using the sol-gel technique, which they suggested to be the cause of RTFM in Mn-doped anatase TiO2 thin films. In other papers, the increase in RTFM is attributed to defects and oxygen vacancies in Mn-doped TiO2 thin films and is explained using the BMPs model [24, 25]. Moreover, Sharma et al. [26] also mentioned that Mn-doped TiO2 thin coatings on quartz via spray pyrolysis at room temperature, ferromagnetic ordering is observed in Ti1−xMnxO2 films with x ≥ 0.05, which they attribute to the creation of BMPs. Even though, most of the investigation indicates BMP is the origin of the observed RTFM; the mechanism is not yet been fully established.

Geprags et al. (the references therein) [26] used spin Hall magnetoresistance (SMR) as a tool to probe AFM insulators α-Fe2O3 (hematite) and NiO in bilayer heterostructures with a Pt heavy-metal top electrode. Their results show a suddenly big SMR amplitude of 2.5 × 10−3, which is double the size of that of prototype Y1Fe2O12/Pt bilayers, designing the system especially appealing for room-temperature AFM spintronic applications. They also explain that the interior of AFM materials is magnetic, however, the orientation of their ordered microscopic moments varies depending on the atomic position. Magnetism in AFMs becomes unnoticed from the exterior as a result of the net magnetic moment is zero. It also suggests that if data were saved in antiferromagnetic moments, it would be unaffected by magnetic fields from the outside, moreover, the antiferromagnetic element would have no magnetic effect on its adjacents regardless of the density with which a device’s elements were organized. Another feature that distinguishes AFMs from ferromagnets is their intrinsically high frequencies.

Despite the lack of macroscopic magnetization, AFM materials have become a focus of spintronics research. When compared to ferromagnets, this material class offers two significant advantages; (i) improved scalability and resistance to magnetic field disturbances; and (ii) magnitude scales, more rapid dynamics, and switching times. However, from a utilization standpoint, the absence of macroscopic magnetization and errant fields
clearly necessitates the development of new magnetization control and readout methods. Spin currents were shown to communicate with magnetic sub-lattices that are unique in ferrimagnets and AFMs by means of spin transfer torques. Spin currents can be generated by Spin pumping in magnetoelectric fields at radio frequencies, thermal gradients, and the spincaloric effect, or the spin Hall effect is observed in metals with high spin-orbit interaction.

Computationally, Park et al [27] studied the electronic structure of Co-doped anatase TiO$_2$:Ti$_{1-x}$Co$_x$O$_2$ ($x = 0.0625$ and $0.125$) and transition metal doped TiO$_2$; the linearized muffin-tin orbital (LMTO) banding method was used in both LSDA and LSDA+U+SO. Their findings show that magnetized systems with $3\ \mu_B$ and $3.7\ \mu_B$ local magnetic moments exist in Mn and Fe-doped systems, respectively. They also found that the magnetic properties of the realizable oxygen vacancy near the Co site have a significant influence on the magnetic properties. Errico et al [28] used the full-potential linearized-agumented plane wave (FLAPW) method to investigate rutile TiO$_2$: Ti$_{1-x}$R$_x$O$_2$ ($R = \text{Mn, Fe, Co, Ni, Cu}$). Their results show that Co doping is ferromagnetically oriented while Mn and Fe are antiferromagnetic. Moreover, doping reduces the formation energy of vacancy, as a result, doped systems have additional vacancies than systems that are not doped. These findings support the theory that oxygen vacancies play a significant role in the formation of a magnetic system in doped TiO$_2$.

Haowei et al [29] used density functional theory (DFT) to calculate the electronic and magnetic properties of anatase TiO$_2$ doped with transition metals (V, Cr, Mn, Fe, Co, Ni). They demonstrated that Mn- and Fe- incorporated TiO$_2$ are antiferromagnetically favored and the acceptor and donor defects, respectively, can improve FM. Zhou et al [30] examined the electronic and magnetic properties of Mn- incorporated TiO$_2$ in combination with experimenting and \textit{ab initio} calculation. Their results showed that the TiO$_2$ codoped with Mn and oxygen vacancies has a magnetic moment of $3.415\ \mu_B$ per Ti$_31$MnO$_{63}$ supper cell and that the main magnetic moment originates from the d electrons of the Mn and the oxygen vacancy.

Recently, DFT+U become widely used in transition metal doped oxides to correct self-interaction error (SIE) with different projector functions such as non-orthogonalized atomic orbital (NAO) for Hubbard manifold [4, 31, 32]. There are several suitable projector functions that can be used as a basis for the Hubbard manifold, as described in detail in Timrov et al (references therein) [33]. In particular, they focus on non-orthogonalized atomic orbitals (NAO), orthogonalized atomic orbitals (OAO), and non-orthogonalized Wannier functions (NWF), orthogonalized Wannier functions (OWF), linearized augmented plane wave (LAPW) approaches, and projector augmented wave (PAW) projector functions. Since all of these projector functions are structurally bonded and rely definitely on the location of atoms, an additional term arises when calculating the derivative of the Hubbard energy correction in relation to displacement (Pulay force) or strains (Pulay stress). In the framework of the Hubbard-corrected DFT, the equations for the Pulay forces were previously obtained for NAO, NWF, OWF, and LAPW, and were also extended to OAO in their reference work [33] according to the Loewdin strategy.

The importance of this advancement is that the NAO and OAO stand out due to their ease of implementation and transparency in practice. DFT+U computations using NAO, in particular, have been shown to be precise in simulating numerous features of different materials. Despite this, NAO has a disadvantage because atomic orbitals have long tails that span a large area of space. As a result, these orbitals’ formal occupational numbers are almost certainly exaggerated [34]. These tails are shortened in several NAO-related works [35] (i.e., atomic orbitals are zero outside of the ‘atomic spheres’), as well as in LAPW and PAW-related viewpoints. The clarity of the border-radius at which the projector functions are shortened is somewhat uncertain [36]. This uncertainty has consequences for the final sizes of interest that are calculated [34, 36]. Moreover, when it comes to NAO with lengthy tails, the Hubbard correction is primarily employed two times in the overlay regions between atoms, which could exacerbate bodiless effects in Hubbard corrected DFT computations. These issues can be solved by orthogonalizing all atoms’ atomic orbitals: This ensures that Hubbard corrections are just utilized once to each Hubbard manifold. Furthermore, DFT+U with OAO detects some changes between sites by orthogonalizing one atom’s orbital in comparison to the neighboring positions, bringing DFT+U towards the full DFT+U+V (DFT+U+V is beyond the scope of this work). Therefore, the OAO is a much more appealing option than the NAO, and it has already been noticed that the OAO comes up with more precise energetic values than the NAO.

Herein, we are interested in diluted magnetic semiconductor metal oxide-based oxide (DMSO) in general and the Mn-doped TiO$_2$ material in particular. Furthermore, the spin-polarized density functional theory (DFT) level has been practiced to the majority of the previously described 3d transition metal atoms doped TiO$_2$ (PBE), Hubbard corrected DFT (DFT+U) has lately been popular for correcting the electron self-interaction problem since it undervalues experimental data, such as the electronic band gap. For instance, L.A. Errico \textit{et al} [38] looked at oxygen vacancy in pure relaxed TiO$_2$ (anatase). They did not, however, have unanticipated magnetic properties. To our knowledge, this is the first time we have investigated the orthogonalized atomic projector-assisted DFT+U on Mn-doped TiO$_2$ with the goal of clearly predicting the electronic structures and
magnetic ordering of Mn-doped TiO$_2$ for promising room-temperature DMSO for next-generation spintronic devices.

The key parameters (highlights) to determine the main focus of this work are the Structural, electronic, and magnetic properties of Mn-doped compounds via anatase Ti$_{16-x}$Mn$_x$O$_{32}$ where $x = 1, 2, 3, 4, 6$, \textit{ab initio} calculations of electronic and magnetic properties by Ortho-atomic projector assisted DFT + U, FM ordering and AFM associated with defect and oxygen vacancy, and significant improvement of the system’s $T_c$, $T_N$, and total magnetization.

2. Methodology

2.1. Crystal structure

Anatase, rutile, and brookite are the primary polymorphic forms of TiO$_2$ [37]. Their electronic and optical properties were examined by Landmann and his colleagues [38]. Based on their results, the rutile phase with lattice constants $a = b = 4.59$ Å and $c = 2.96$ Å, and the anatase phase with lattice constants $a = b = 3.78$ Å, and $c = 9.52$ Å crystallize in tetragonal symmetry and the brookite phase, on the other hand, has orthorhombic symmetry and lattice parameters $a = 9.16$ Å, $b = 5.43$ Å, and $c = 5.13$ Å. The tetragonal symmetry of the investigated compound (anatase phase TiO$_2$) was taken from the open database of the Resource Material Project [39].

The crystal structure under consideration has the lattice parameters $a = b = 3.8027$ Å and $c = 9.747752$ Å and is symmetrical within the space group $I = I4_1$/amd. Tetragonal TiO$_2$ contains four Titanium (Ti) and eight Oxygen (O) atoms in its conventional unit-cell. A six-O atom rotates and is positioned symmetrically to the entire Ti in the case of the octahedral polygon (TiO$_6$)

The computations were performed using a supper cell of TiO$_2$ volume structure with sixteen Titanium and thirty two Oxygen atoms, which consisted of $2 \times 2 \times 1$ duplicates. A similar supercell has been used to form the Mn-doped TiO$_2$ system with concentrations of (Ti$_{16-x}$Mn$_x$O$_{32}$) where $x = 1, 2, 3, 4$ and 6

2.2. Computational details

For all calculations, the pseudopotential approach for plane waves (PW) was used as applied in the distribution of QUANTUM ESPRESSO [40–42]. The exchange correlational (xc) function was built with GGA using the PBE prescription [43], and the ultrasoft pseudopotentials are chosen with reference to the SSSP library 1.1 [44]. The total energy was calculated using cutoff energy for plane waves of 680 eV and optimized the geometry. Brillouin zone integration is carried out using $7 \times 7 \times 1$ (Monkhorst–Pack, MP) [45].

For the calculations of DFT + U, we used the simplified rotational invariant formulation and also ortho atomic orbitals, and the method of Lowdin orthogonalization as reported in [33] as Hubbard manifold projectors. The linear response technique [46], as implemented in DFPT [47], was used to compute the Hubbard U-parameters. We employ uniform $\Gamma$-centered $k$- and $q$-point meshes with sizes $3 \times 3 \times 3$ and $3 \times 3 \times 3$, respectively, which yields a calculated value of $U$ with a precision of 0.1 eV. We also calculated $U$ using the self-consistent method as reported in detail in [48], which includes cyclic computations with structural optimizations and recomputation of the Hubbard parameters for every new geometry. We obtained $U = 6.83$ eV for the Mn(3d) state using the DFT + U framework.

3. Results and discussion

3.1. Geometric, lattice parameter optimizations, and effect of oxygen vacancy

To investigate defects and the effect of oxygen vacancy, we have used five different concentrations in the $2 \times 2 \times 1$ TiO$_2$ supper cell. As table 1 indicates, the lattice constants and the volumes of the system decrease with the PBE functional. In contrast, for PBE + U, both the lattice constants and the volume are increasing. As a result, including the Hubbard parameter corrects the SIE. Moreover, the volume change of PBE + U compared to the pristine supper cell ($V_{PBE} + UC$) is the volume of the doped supper cell and $V_{PBE} + UC$ (obtained from our previous work [4]) is the volume of the pristine supper cell, the change in volume increased from $3.947$ Å$^3$ to $24.15$ Å$^3$ with increasing concentration. Table 1 shows the calculated lattice parameters and the volumes of the supper cell for Mn (2.08, 4.17, 6.25, 8.33, and 12.5%) concentrations from its crystal structure. The result shows that for 2.08%, $a \Rightarrow b = 7.5858$ Å, and $c = 9.637$ Å, and shows that the lattice parameters are larger than that of the pristine (PBE + U). From the table for the calculation of the radii by R.D. Shannon [49], it can be seen that the radii of Mn$^{2+}$ and Ti$^{4+}$ are (0.67 and 0.61 Å, respectively). It is clear that Mn replaces Ti in Ti$_{16}$O$_{32}$, leading to an expansion of the $a \Rightarrow b$ on some concentrations and $c$ lattice parameters in others due to the larger ion size. It was also found that the volume of the supper cell increased from 540.62 Å$^3$ (pristine PBE + U) to 554.567 Å$^3$ (2.08% of Mn-doped PBE + U). Moreover, the calculated lattice parameters for
a Mn concentration of 4.17% are \( a = b = 7.644 \) Å and \( c = 9.5759 \) Å, for a doping of 6.25%, \( a = b = 7.6797 \) Å and \( c = 9.5431 \) Å, for doping of 8.33%; \( a = b = 7.7058 \) Å and \( c = 9.5112 \) Å, for doping of 12.5%; \( a = b = 7.65 \) Å and \( c = 9.5521 \) Å, respectively (table 1). Furthermore, at 4.17%, 6.25%, 8.33%, and 12.5% are 561.234 Å\(^3\), 562.831 Å\(^3\), 559.012 Å\(^3\), and 564.77 Å\(^3\) respectively the volume of the super cells. Thus, the increase in volume could be because of the replacement of the manganese in place of titanium because the Mn \( 2+ \) radius is greater as compared to Ti \( 4+ \) ion. Furthermore, the substitution of tetravalent Ti\( 4+ \) by Mn\( 2+ \) necessitates the elimination of two electrons from the lattice to counterbalance the charge disparity, resulting in an oxygen vacancy for local charge balance. Electrons are discharged into the system when a nearby oxygen atom is released from the substituted Mn into the TiO\(_2\) supper cell. Therefore, as Mn doping increases, the concentration of oxygen vacancies in the doped TiO\(_2\) lattice is also expected to increase, as more Mn\(^{2+}\) will replace the Ti\(^{4+}\) and the presence of Mn\(^{2+}\) in high concentrations improves the system’s ferro and antiferromagnetic properties while also inducing impurity energy levels (IEL) due to oxygen 2p and Mn 3d hybridization, resulting in a significantly reduced band gap and facilitated electron transport in agreement with [22, 50].

Figures 1–5 illustrate the supercell of Mn-doped TiO\(_2\) (Ti\(_{16-x}\)Mn\(_x\)O\(_{32}\), where \( x = 1, 2, 3, 4, \) and 6), and figure 6 indicates the sample detached from these figures before (6(c)) and after (6(a), and (b)) geometric relaxation respectively. Moreover, figures 1(a), 2(a), 3(a), 4(a), and 5(a) shows after self consistent field calculation while figures 1(b), 2(b), 3(b), 4(b), and 5(b) indicates after geometrical optimization with different concentration. The former figures revealed that all the substituted Mn atom is rotated by six oxygen atom (see figure 6(c)); four of which are nearest (\( x_1 = x_2 = y_1 = y_2 = 1.9488 \) Å) and two of which are farthest (\( x_2 = z_2 = 2.0096 \) Å) from Mn ion for all concentration (see table 2). Hence, the Mn-doped TiO\(_2\)’s with different concentrations after self-consistent field calculations are symmetric and all of them have an equal

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Table 1. Computed lattice constants and volumes for pure and Mn replaced TiO\(_2\) employing PBE and PBE + U functionals.

| Compound          | \( a = b \) (PBE) | \( c \) (PBE) | V(PBE) | \( a = b \) (+U) | \( c \) (+U) | V(+U) | \( V_{scf(+U)} \)-\( V_{p(+U)} \) | Values       |
|-------------------|-------------------|----------------|--------|-----------------|---------------|--------|---------------------------------|-------------|
| Ti\(_4\)O\(_8\)    | 3.743             | 9.302          | 135.92 | 9.502           | 135.92        | 5.27   |                                | Experi. [51]|
| Ti\(_{16}\)O\(_{32}\) | 7.6054           | 9.7478         | 563.83 | 9.7478          | 563.83        | 563.83 |                                | Mater. Proj.|
| Ti\(_{12}\)Mn\(_6\)O\(_{32}\) | 7.5903           | 9.5443         | 549.872| 7.6444          | 9.5799        | 561.234|                                | 22.21 calculated|
| Ti\(_{10}\)Mn\(_3\)O\(_{32}\) | 7.5901           | 9.5444         | 549.849| 7.6444          | 9.5799        | 561.234|                                | 22.21 calculated|
| Ti\(_{15}\)Mn\(_1\)O\(_{32}\) | 7.5901           | 9.5444         | 549.849| 7.6444          | 9.5799        | 561.234|                                | 22.21 calculated|

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Figure 1. Ti\(_{16-x}\)Mn\(_x\)O\(_{32}\) for \( x = 1 \) suppercell after (a) Self consistent field (scf) calculation, and (b) Geometrical optimization (vc-relax).
number of bonds (six), and a similar coordination number (octahedral). However, after relaxation as it is shown in figures 1(b), 2(b), and 3(b) some of the bonds were broken. For instance, in the case of 2.08% of Mn; two of the O-Mn (x2 and y2) bonds were broken and the number of bonds was reduced to 4 and its coordination number becomes tetragonal (as in figure 1(b) and more clearly 6(a)). Furthermore, when concentration increased to 4.17% and 6.25% the number of bonds around every Mn ion (x2) was broken and reduced to five (as in figures 2(b), 3(b), and clearly as it appears in 6(b)). Thus, their coordination numbers are trigonal bipyramid. On the contrary, when the concentration of Mn increased to 8.33% and then 12.5%; there was no bond broken and their coordination number was not changed (see figures 4 and 5). Moreover, the result from table 3 indicates the x and y axes bond lengths are relaxed from $x_1 = 1.9488 \text{ Å}$ to $1.9598 \text{ Å}$, $y_1 = 1.9488 \text{ Å}$ to $1.9598 \text{ Å}$ for 2.08%, and $x_1 = 1.9488 \text{ Å}$ to $1.9558 \text{ Å}$, $y_1 = y_2 = 1.9488 \text{ Å}$ to $1.9591 \text{ Å}$ for both Mn atom in 4.17% while in the z-axis; bond lengths reduced from $z_1 = 2.0096 \text{ Å}$ to $1.9414 \text{ Å}$, $z_2 = 2.0096 \text{ Å}$ to $1.9888 \text{ Å}$ for 1st and 2nd Mn ion respectively. However, form 6.25% Mn; for the first and second atom of the Mn-O bonds; the x and y axes bond length increased from $x_1 = 1.9488 \text{ Å}$ to $1.9574 \text{ Å}$, $y_1 = 1.9488 \text{ Å}$ to $1.9514 \text{ Å}$, $y_2 = 1.9488 \text{ Å}$ to $1.9772 \text{ Å}$ for 1st and
2nd atoms, respectively. However, the z-axis reduced from $z_1 = 2.0096$ Å to 1.9945 Å, $z_2 = 2.0096$ Å to 1.9668 Å for the 1st and 2nd Mn atoms, while for the 3rd atom $x$ and $y$ axes bond length increased $x_1 = 1.9488$ Å to 1.9617 Å, $y_1 = y_2 = 1.9488$ Å to 1.9681 Å, and z axis reduced from $z_1 = 2.0096$ to 1.9947, $z_2 = 2.0096$ to 1.9636 Å. Moreover, for 8.33% Mn atom, for all the four atoms of Mn, the nearest bond between Mn and O relaxed uniformly from 1.9488 Å to 1.9561 Å, and the next nearest reduced from 2.0096 Å to 1.9693 Å. Thus, in this case, the system is symmetric but there is a change in volume. However, when the concentration increased to 12.5% in the first four nearest atoms $x_1 = 1.9488$ reduced to 1.9457 and $x_2 = 1.9488$ Å relaxed to 1.9841 Å also $y_1 = y_2 = 1.9488$ Å relaxed to 1.9564 Å however, in the next nearest bond (z-axis) reduces from $z_3 = 2.0096$ to 1.9903 Å and $z_2 = 2.0096$ to 1.9680 Å. Moreover, the 5th and 6th atoms $x_1$, $x_2$, $y_1$, and $y_2$ relax however, $Z_1$ and $Z_2$ are reduced.

Figure 4. $\text{Ti}_{16-x}\text{Mn}_x\text{O}_{32}$ for $x = 4$ supercell after (a) Scf calculation and (b) Geometric optimization.

Figure 5. $\text{Ti}_{16-x}\text{Mn}_x\text{O}_{32}$ for $x = 6$ supercell after (a) Scf calculation and (b) Geometric optimization.
As a result, our findings confirm the emergence of Oxygen vacancies in the TiO2 lattice when Mn with small valence ions are replaced by larger valence Ti4+ ions to achieve charge neutrality within the lattice. When an electron is caught in Oxygen vacancies, the vacancies are coupled with the magnetic moments of Mn in their hydrogen-like orbit around the vacancies, resulting in the formation of a bound magnetic polaron. If there are enough BMPs, two of them may overlap, resulting in a type of long-range FM ordering in the oxide lattice. As the number of replaced Mn ions increases, the concentration of BMPs also increases, and thus, the likelihood of their overlap should rise, this leads to improved FM ordering in the lattice in agreement with [2, 50].

We also investigated the effect of oxygen vacancy in both pristine and Mn-doped systems by removing one oxygen atom. For example, in the relaxed pristine (Ti16O31) case, we obtained a non-zero magnetic moment and total magnetization was calculated to be 2.00 μB, indicating that the material has magnetic properties. Unfortunately, L.A. Errico et al [28] did not obtain a magnetic moment for the pristine oxygen vacancy of a relaxed anatase structure (Ti16O31). This difference indicates that the system is being influenced by the ortho-atomic projector. Moreover, for the Mn-doped case; we have considered both the non-vacant and vacant cases of different concentrations. Thus, we have found 3 μB in agreement with the result obtained by [27] for non-vacant Ti14MnO32, and 5 μB and 3.67 μB for oxygen vacancy near Ti and Mn, respectively. Furthermore, for non-vacant Ti14Mn3O32 the total magnetization was 2.85 μB/Mn, and vacancy near Ti and Mn total magnetization was 3.98 μB/Mn and 3.75 μB/Mn respectively. Also for non-vacant Ti13MnO32 the total magnetization was calculated to be 3.04 μB/Mn, however, for the vacant case total magnetization was 3.67 μB/Mn for both near Ti and Mn. Moreover, for the non-vacant Ti13MnO32 the total magnetization of 2.88 μB/Mn but for the vacant case 3.48 μB/Mn and 3.41 μB/Mn near Ti and Mn, respectively. For Ti13Mn6O32 case, the total magnetization was calculated to be 2.93 μB/Mn, however, for the vacant case the total magnetization was calculated to be 3.32 μB/Mn and 3.28 μB/Mn, respectively. Hence, the result shows oxygen vacancy in all pristine and doped cases, the average total magnetization is enhanced. On the other hand, in all our systems oxygen vacancy near Ti is better and affected by the oxygen vacancy than near Mn. Hence, the result shows oxygen vacancy plays important role in increasing the magnetization of our system and BMPs are the sources of magnetization. [21, 24, 25].

3.2. Formation energy and structural stability

In this work, we are going to calculate the change in magnetic energy and critical temperature. For that matter, we need to calculate both the FM and the AFM of the supercell. Thus, we have considered only 4.17%, 8.33%, and 12.5% of Mn concentration at their symmetric position. Hence, the structural stability of doped TiO2 with 4.17%, 8.33%, and 12.5% Mn concentrations was confirmed using formation energy calculations. To compute the formation energy, equation (1) is employed;

\[
E_{\text{form}} = E(\text{Mn}, \text{TiO}_2) - E(\text{TiO}_2) - \sum_i n_i (\mu_{\text{Mn}} - \mu_{\text{Ti}})
\]  

Figure 6. The coordination number of Mn-doped TiO2 in (a) Tetragonal, (b) Trigonal bipyramid, and (c) octahedral after geometric optimization.
where $E_{\text{form}}$ is the formation energy, $E(\text{Mn, TiO}_2)$ and $E(\text{TiO}_2)$ is the total amount of energy of the doped and pristine TiO$_2$, respectively, $n_i$ is the total number of atoms substituted on the cation site, and the calculated chemical potential of Mn and Ti are denoted by $\mu_{\text{Mn}}$ and $\mu_{\text{Ti}}$, respectively. The growth circumstances, which could be either Ti- or O-rich, have an effect on the formation of energy.

In this way, the chemical potentials of TiO$_2$ ($\mu_{\text{TiO}_2}$), Ti ($\mu_{\text{Ti}}$), and O ($\mu_{\text{O}}$) can satisfy the formula $\mu_{\text{TiO}_2} = \mu_{\text{Ti}} + 2\mu_{\text{O}}$. The total amount of energy of an O$_2$ molecule, $\mu_{\text{O}} = \frac{1}{2}E(\text{O}_2)$, is used to calculate $\mu_{\text{O}}$ in the

| Conc. of Mn | Bond length after relaxation (angstrom) | Number of bonds | Co-ordination |
|------------|---------------------------------------|----------------|--------------|
| x-axis     | y-axis                                | z-axis         |              |
| 2.08%      | $x_1 = 1.9488$ $y_1 = 1.9488$ $z_1 = 2.0096$ | 6              | octahedral (see figure 4(c)) |
| 4.17%      |                                       |                |              |
| 6.25%      |                                       |                |              |
| 8.33%      |                                       |                |              |
| 12.5%      |                                       |                |              |

Table 2. Calculated bond length, number of bonds, and coordination number in different concentrations of Mn-doped TiO$_2$ after SCF calculation.
Table 3. Calculated bond length, number of bonds, and coordination number in different concentrations of Mn–doped TiO$_2$ after geometric optimization.

| Conc. of Mn | Bond length after relaxation (angstrom) | Number of bonds | Co-ordination |
|-------------|----------------------------------------|----------------|---------------|
|             | x-axis       | y-axis       | z-axis       |               |
| 2.08%       | X$_1$ = 1.9598 | Y$_1$ = 1.9598 | Z$_1$ = 1.9313 | 4 | Tetrahedral (see figures 4(a)) |
|             | X$_2$ = no bond | Y$_2$ = no bond | Z$_2$ = 2.0372 |               |
| 4.17%       | X$_1$ = 1.9538 | Y$_1$ = 1.9591 | Z$_1$ = 1.9414 | 5 | Trigonal bi-pyramidal (see figure 4(b)) |
|             | X$_2$ = no bond | Y$_2$ = 1.9591 | Z$_2$ = 1.9888 |               |
| 6.25%       | X$_1$ = 1.9574 | Y$_1$ = 1.9514 | Z$_1$ = 1.9945 | 5 | Trigonal bi-pyramidal |
|             | X$_2$ = no bond | Y$_2$ = 1.9772 | Z$_2$ = 1.9668 |               |
| 8.33%       | X$_1$ = 1.9561 | Y$_1$ = 1.9561 | Z$_1$ = 1.9693 | 6 | octahedral |
|             | X$_2$ = 1.9561 | Y$_2$ = 1.9561 | Z$_2$ = 1.9693 |               |
| 12.5%       | X$_1$ = 1.9457 | Y$_1$ = 1.9564 | Z$_1$ = 1.9903 | 6 | octahedral |
|             | X$_2$ = 1.9441 | Y$_2$ = 1.9564 | Z$_2$ = 1.9680 |               |

O–rich growth state, and $\mu_{Ti}$ is calculated by the formula $\mu_{Ti} = \mu_{TiO_2} - 2\mu_{O}$, $\mu_{Ti}$ is the energy of a Ti atom in bulk titanium, as well as $\mu_{O}$ is computed by $\mu_{O} = \frac{\mu_{TiO_2} - \mu_{Mn}}{2}$, also $\mu_{Mn}$ is the energy of a Mn atom in bulk Manganese in the Ti-rich growth environment.

For Titanium- and Oxygen-rich circumstances, table 4 summarizes formation energy for Mn-doped TiO$_2$ at varying concentrations. The Oxygen-rich condition was shown to be more advantageous than the Titanium-rich condition based on the three different doping concentration levels.
Thus, our findings suggest that Mn doping is advantageous both energetically and structurally in an Oxygen-rich environment. This suggests that replacing Ti with Mn saves more energy in Oxygen-rich growth conditions than in Titanium-rich growth conditions. This indicates synthesis of the Mn-doped TiO$_2$ with a higher level of doping in the experiment would be reasonably simple in Oxygen-rich conditions [4, 53–55].

### 3.3. Electronic structures and magnetic properties

We studied the impact of Mn concentrations on the electronic and magnetic properties of 4.17, 8.33, and 12.5 percent Mn-doped TiO$_2$ at a symmetric position. The total DOS (density of state) both for FM and AFM PBE+U functionals were used to compute the electronic structural properties of Mn-doped systems (see figure 7). It has been shown in [4] that for pure TiO$_2$ systems, the essence of the density of states for spin-up and spin-down channels are symmetric, indicating non-magnetic properties. As indicated in figure 7, column (i) is DOS of FM while column (ii) is AFM. The computation revealed a substantial difference in the majority (spin up) and minority (spin down) states both in magnitude and number of added peaks near the conduction band for both FM and AFM Mn-doped systems with concentrations of 4.17, 8.33, and 12.5%, (see figures 7(a)–(f)). Moreover, in figures 7(a), (b), (c), and (d) the majority and minority spin channels are antisymmetric, indicating that they have magnetic properties. They also show spin polarization. However, figures 7(e) and (f) show null spin polarization and are symmetric. These symmetric properties indicate the AFM system with 8.33 and 12.5% Mn

| Compound     | Mn (percentage) | Oxygen-rich | Titanium-rich | Fermi energy  |
|--------------|----------------|-------------|--------------|---------------|
| pure         | —              | —           | —            | 8.9744        |
| 2Mn-doped    | 4.17           | −30.14      | −14.64       | 6.8538        |
| 4Mn-doped    | 8.33           | 47.53       | 78.52        | 6.91          |
| 6Mn-doped    | 12.5           | 124.84      | 171.31       | 6.857         |

Figure 7. Plots of DOS for Mn dopant in TiO$_2$ Ferromagnetic (a) Ti$_{16-x}$Mn$_x$O$_{32}$ for $x = 2$, (b) Ti$_{16-x}$Mn$_x$O$_{32}$ for $x = 4$, and (c) Ti$_{16-x}$Mn$_x$O$_{32}$ for $x = 6$, Antiferromagnetic (d) Ti$_{16-x}$Mn$_x$O$_{32}$ for $x = 2$, (e) Ti$_{16-x}$Mn$_x$O$_{32}$ for $x = 4$, and (f) Ti$_{16-x}$Mn$_x$O$_{32}$ for $x = 6$ systems.
concentrations has non-magnetic properties. Furthermore, except in figure 7(d), that is an n-type (which has a low effective mass than p-type) semiconductor and hence, it has high conductivity [56] and the rest are p-type semiconductors. Hence, the result confirms that all of them exhibit metallic properties.

As shown in reference [4], in the PBE+U calculation of pristine TiO₂, the band gap is 3.23 eV, which is in agreement with the existing experimental results [57]. However, when 4.17% Mn was doped, the band gap was reduced to 2.21 eV with a slight change in the band edges (see figure 8(a)). When the concentration increases to 8.33%, the band gap energy decreases to 2.13 eV (see figure 8(b)), as well as modest alterations to the band’s edges. When the impurity level increases to 12.5%Mn, the predicted band gap decreases to 1.69 eV (see figure 8(c)), and the band edge shifts slightly, bringing the Fermi level closer to the valence band maximum (VBM). Thus, doping Mn in TiO₂ reduces the bandgap while also improving system conductivity for spintronic applications and photocatalytic performance [58]. Furthermore, as can be seen from the calculated band structures, additional impurity levels were formed between the VBM and the conduction band minimum (CBM), and also an indirect bandgap structure was observed in all cases. The calculated values of the band gap energy agreed with the experimental result [50].

Figures 9(a), (b), (c) and (d) show the PDOS (partial density of states) of the Mn-doped system for FM (figures 9(a) and (c)) and AFM (figures 9(b) and (d)) of 8.33% and 12.5% and the contribution of each orbital. The figures show that oxygen 2p in the valence band and titanium 3d in the conduction band contribute more. Moreover, oxygen 2p and Mn 3d hybridize between the VBM and CBM. This induced an impurity energy level and reduced the band gap of the system. It was also found that both the size of the PDOS and the number of peaks between VBM and CBM increased with increasing concentration. Thus, figures 8 and 9 show the reduction of the band gap energy as a result of the impurity of the system, which is very useful for various electronic and energy generation applications [58]. Furthermore, our PDOS calculation also confirms the AFM system of 8.33% and 12.5% concentrations of Mn show non-magnetic while the FM systems exhibit magnetic properties.

3.4. Magnetic interaction in Mn-doped TiO₂

To investigate if the impurities in the supercell tended to align ferromagnetically or antiferromagnetically, we did simulations with two, four, and six impurities in the supercell, considering aligned spins or not. Table 5 depicts the energy change for FM and AFM states. The overall energy variation within FM and AFM
arrangement may be connected to the exchange coupling constants $J_{ij}$ between dopants at positions $i$ and $j$, as well as the critical temperature, utilizing a basic Ising model. The system’s total energy in a given magnetic state could be calculated as

$$E = -\sum_{ij} J_{ij} S_i S_j$$

(2)

where $S_i$ and $S_j$ are the spins of the dopants at positions $i$ and $j$, respectively, and the sum runs over all dopants up to a particular adjacent shell. It is possible to determine some of the exchange parameters by calculating the total energy differences $\Delta E = E_{FM} - E_{AFM}$ for various impurity distributions. The number of $J_{ij}$’s that can be estimated is determined by the quantity of distinct magnetic structures which could be established in self-consistent calculations with a small unit cell [28].

Hence, the magnetic interaction of Mn-doped TiO$_2$ (Ti$_{16-x}$Mn$_x$O$_{32}$ for $x = 2, 4, 6$) systems was investigated by calculating the difference in total energy within ferromagnetic (FM) and antiferromagnetic (AFM) arrangements at different Mn concentrations and doping site using equation (3);

$$\Delta E = E_{FM} - E_{AFM}$$

(3)

where $E_{FM}$ and $E_{AFM}$ are the supercell’s total ground state energy in FM as well as AFM conditions, correspondingly [59].

### 3.5. Room temperature ferro- and antiferromagnetism

Our result from table 5 indicates that the antiferromagnetic property of the system is stable for 4.17% Mn, whereas ferromagnetic order favors the remainder of the case. It also revealed that as the concentration rises, the amount of charge increases proportionally. Furthermore, the charge on Ti and Mn ions increased relative to pristine TiO$_2$ whereas the charge on oxygen ions is reduced as concentration increases. Hence, there is a charge transfer from oxygen to the rest of the ions, inducing a magnetic moment per atom in the system. Nevertheless, our indicates that the magnetic moment increased according to the amount of dopant considered for both the FM and AFM systems. Furthermore, Titanium and Oxygen also contribute to the total magnetization of the system. As a result, the impurity concentration has an impact on the system’s magnetic characteristics [4, 28].

We also estimated the antiferromagnetic system’s Neel temperature ($T_N$) and the ferromagnetic system’s ferromagnetic transition temperature ($T_c$). The Heisenberg-Hamiltonian model was mapped with the mean-
the cation site of the system, Δ

Where equation (\[\text{concentration}\]) in our discussion of part 2A and table 3 result above, we have seen that there is no bond broken result, we have observed that the critical temperature is below room temperature for 8.33% of Mn concentration, the critical temperature is 385.63 K which is above room temperature. From this during geometric relaxation, and also the symmetry of low concentration of oxygen vacancy. Hence, the reduction of T

change in volume with respect to the others is small. This indicates the system has a low defect and results in a

temperature antiferromagnetism. Nonetheless, because percolation is known to influence magnetic ordering in Mn substituted TiO\(_2\) systems, the modified systems’ T\(_c\) is overestimated by the mean-field approximation, which cannot capture this feature [61]. To address this problem, the empirical relationship between the mean field value of the curie/Neel temperature and the corrected curie/Neel temperature (T\(_c\)\text{corr} = (0.506) T\(_c\)\text{MFA}) [60] is used, where T\(_c\)\text{MFA} is the Curie/Neel temperature calculated using equation (4).

Our result shows there is a fluctuation between AFM and FM as concentration increases from 4.17% to 8.33%. Table 5 indicates that the Neel temperature was calculated by manipulating equation (4) and using the critical/Neel temperature correction, T\(_N\) was calculated to be 804.13 K for Mn concentration of 4.17% and critical temperature 255.42 K for 8.33% of Mn concentration which is below room temperature. Moreover, for 12.5% of Mn concentration, the critical temperature is 385.63 K which is above room temperature. From this result, we have observed that the critical temperature is below room temperature for 8.33% of Mn concentration. In our discussion of part 2A and table 3 result above, we have seen that there is no bond broken during geometric relaxation, and also the symmetry of figure 4 has not changed. In addition from table 1, the change in volume with respect to the others is small. This indicates the system has a low defect and results in a low concentration of oxygen vacancy. Hence, the reduction of T\(_c\) is most probably from a low concentration of BMPs, indicates the number of substituted atoms on the cation site of the system, T\(_c\)\text{MFA} is the curie temperature as approximated by a mean field, and k\(_B\) denotes the Boltzmann constant.

Nonetheless, because percolation is known to influence magnetic ordering in Mn substituted TiO\(_2\) systems, the modified systems’ T\(_c\) is overestimated by the mean-field approximation, which cannot capture this feature [61]. To address this problem, the empirical relationship between the mean field value of the curie/Neel temperature and the corrected curie/Neel temperature (T\(_c\)\text{corr} = (0.506) T\(_c\)\text{MFA}) [60] is used, where T\(_c\)\text{MFA} is the Curie/Neel temperature calculated using equation (4).

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**Table 5.** Calculated charge, magnetic moment (average for Ti and O), change in energy, FM transition, and AFM (Neel) temperature based on Mn dopant in percentage.

| Site            | arrangement | %Mn | charge     | \(\mu_{\text{BREM}}\) | \(\mu_{\text{BAFM}}\) | \(\Delta E (eV)\) | \(T_{c,\text{MFA}}(K)\) | \(T_{c,\text{corr}}(K)\) |
|-----------------|-------------|-----|------------|------------------------|------------------------|------------------|------------------------|------------------------|
| pristine        | —           | —   | 0.00       | 0.00                   | 0.00                   | 0.00             | 0.00                   | 0.00                   |
| Ti              | —           | —   | 8.4789     | 0.00                   | 0.00                   | 0.00             | 0.00                   | 0.00                   |
| O               | —           | —   | 5.0490     | 0.00                   | 0.00                   | 0.00             | 0.00                   | 0.00                   |
| 2Mn-doped       | symmetric   | —   | —          | —                      | —                      | 0.3945           | 1589.18                | 804.13                 |
| Mn\(_1\)        | symmetric   | 4.17| 11.7684    | 3.2651                 | -3.2084                | —                | —                      | —                      |
| Mn\(_2\)        | symmetric   | 4.17| 11.7710    | 3.2591                 | 2.4457                 | —                | —                      | —                      |
| Ti              | —           | —   | 8.4213     | 0.0079                 | 0.0028                 | —                | —                      | —                      |
| O               | —           | —   | 5.3461     | -0.058                 | -0.0223                | —                | —                      | —                      |
| 4Mn-doped       | symmetric   | —   | —          | —                      | —                      | -0.2613          | 504.783                | 255.42                 |
| Mn\(_1\)        | symmetric   | 8.33| 11.8270    | 3.3308                 | -3.3000                | —                | —                      | —                      |
| Mn\(_2\)        | symmetric   | 8.33| 11.8270    | 3.3308                 | 3.3002                 | —                | —                      | —                      |
| Mn\(_3\)        | symmetric   | 8.33| 11.8270    | 3.3308                 | -3.3000                | —                | —                      | —                      |
| Mn\(_4\)        | symmetric   | 8.33| 11.8270    | 3.3308                 | 3.3002                 | —                | —                      | —                      |
| Ti              | —           | —   | 8.5008     | 0.02                   | 0.006                 | —                | —                      | —                      |
| O               | —           | —   | 5.4039     | -0.12                  | -0.06                 | —                | —                      | —                      |
| 6Mn-doped       | symmetric   | —   | —          | —                      | —                      | -0.5916          | 762.106                | 385.63                 |
| Mn\(_1\)        | symmetric   | 12.5| 11.7583    | 3.3265                 | -3.3510                | —                | —                      | —                      |
| Mn\(_2\)        | symmetric   | 12.5| 11.7583    | 3.3265                 | 3.3511                 | —                | —                      | —                      |
| Mn\(_3\)        | symmetric   | 12.5| 11.8117    | 3.3825                 | -3.3510                | —                | —                      | —                      |
| Mn\(_4\)        | symmetric   | 12.5| 11.8117    | 3.3825                 | 3.3510                 | —                | —                      | —                      |
| Mn\(_5\)        | symmetric   | 12.5| 11.8117    | 3.3825                 | -3.2504                | —                | —                      | —                      |
| Mn\(_6\)        | symmetric   | 12.5| 11.8117    | 3.3825                 | 3.2504                 | —                | —                      | —                      |
| Ti              | —           | —   | 8.4924     | 0.023                  | 0.004                 | —                | —                      | —                      |
| O               | —           | —   | 5.33       | -0.18                  | -0.017                | —                | —                      | —                      |
The outcomes of this work revealed that the ferromagnetism and antiferromagnetism tunability could be achieved by varying the concentration of magnetic dopant. Furthermore, the calculated Neel temperature \( T_N \) and curie temperature \( T_c \) in table 5 were found to be above RT for 4.17% and 12.5% of Mn, respectively, revealing that the Mn-doping TiO\(_2\) is one of the auspicious DMOS materials for spintronic applications.

4. Conclusion

We conducted an extensive investigation of the electronic structure, structural formation energy, crystal, magnetic properties, ferromagnetic transition temperature \( T_N \), and Neel temperature \( T_N \) of the system of Mn-doped anatase TiO\(_2\) supercell for different concentrations. We applied an ortho-atomic projector-assisted DFT \(+U\) method to capture some corrections between sites by orthogonalizing the orbitals of one atom in combination with those of the neighboring sites and to correct self-interaction error (SIE) by utilizing Hubbard’s effective \( U \) value of 6.83 eV for Mn (3d). The incorporation of Mn at different concentrations causes the bond between Mn and O to break and also changes the bond length. This results formation of defects and oxygen vacancies that change properties of the system, such as volume change (15.947 to 24.15 Å\(^3\) for 2.08%–12.5% Mn dopant concentration in PBE + U), bandgap narrowing from 3.23 eV to 2.21 eV (for 4.17% of Mn), 2.13 eV (for 8.33% of Mn) and 1.69 eV (for 12.5% of Mn) as indicated in electronic band structure graphs, magnetic properties (FM and AFM obtained from formation energy calculation), semiconducting properties (n-type and p-type) as indicated in DOS calculation, \( T_N \) (changes from 255.42 K (for 8.33% of Mn) to 385.63 K (for 12.5% of Mn) and \( T_N \) calculated to be 804.13 K (for 4.17% of Mn) for various spintronic applications. We have also shown oxygen vacancy for pristine (in the relaxed pristine (Ti\(_{10}\)O\(_{31}\)); we obtained a non-zero magnetic moment and total magnetization of 2.00 \( \mu_B \) which shows the effect of the ortho-atomic projector), and total magnetization of oxygen vacancy near Ti and Mn, respectively, for Ti\(_{12}\)Mn\(_{0}\)O\(_{31}\) are (5 \( \mu_B \) and 3.67 \( \mu_B \)), Ti\(_{14}\)Mn\(_{2}\)O\(_{31}\) (3.98 \( \mu_B \)/Mn and 3.75 \( \mu_B \)/Mn), Ti\(_{13}\)Mn\(_{3}\)O\(_{31}\) (3.76 \( \mu_B \)/Mn and 3.41 \( \mu_B \)/Mn), and Ti\(_{10}\)Mn\(_{6}\)O\(_{31}\) (3.32 \( \mu_B \)/Mn and 3.28 \( \mu_B \)/Mn) and shows enhanced magnetization, indicating that the material has magnetic properties. Moreover, when Mn\(^{2+}\) is substituted in terms of Ti\(^{4+}\), Mn\(^{2+}\) distorts the lattice; and as a result of charge state differences, oxygen vacancies are produced to preserve charge neutrality. Thus, the presence of Mn\(^{2+}\) at various concentrations within the framework raises the number of oxygen vacancies and thus BMP, which raises \( T_N \) and \( T_c \). The large difference between calculated \( T_N \) and \( T_N \) values indicates the amount of defect site confined electrons, which influences the magnetism of Mn-doped TiO\(_2\) systems. Hence, our findings suggest that TiO\(_2\) could be tailored through doping transition metal and oxygen vacancy mediated diluted magnetic oxide semiconductors for promising spintronic applications.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Conflicts of interest

There are no conflicts to declare.

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