Effect of transition metal (TM) doping on structural and magnetic properties in hexagonal YMn$_{0.917}$TM$_{0.083}$O$_3$ systems

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Abstract

Suitable TM doping at the Mn site is an important access to manipulate magnetic properties of hexagonal YMnO$_3$, however, it has not yet been systematically explored how the strength of antiferromagnetic interactions and the magnetic transition temperatures ($T_N$) are modified in the doping YMn$_{0.917}$TM$_{0.083}$O$_3$ systems. In the work, we have performed first-principles calculations to study the effect of TM doping on the structural and magnetic properties of hexagonal YMn$_{0.917}$TM$_{0.083}$O$_3$ bulks; the results are combined with the available experimental results. The calculated results reveal that the planar TM-O bonds and O-TM-O angles of TMO$_5$ bipyramid are both prominent structural features for the transformations of magnetic properties. We have also predicted the Ti, V, Cr and Fe doping effects on magnetic properties and further analyzed the TM electronic structures of TMO$_5$ bipyramid in the YMn$_{0.917}$TM$_{0.083}$O$_3$(001)/MgO(001) film configurations, which could provide more understanding towards the designing of new generation multifunctional devices.

Keyword: Condensed matter physics
1. Introduction

Multiferroic materials exhibit simultaneous ferroic responses with coupled electric, magnetic, and structural orders. They are very important because of their unique and strong coupling of electric and magnetic properties, giving rise to the simultaneous presence of more than one ferroic property. Hexagonal YMnO$_3$ is the most extensively studied multiferroic material among all hexagonal manganites [1], which possesses magnetism and ferroelectricity simultaneously with a high ferroelectric transition temperature ($\sim$ 900 K) and a low antiferromagnetic (AFM) transition temperature ($\sim$ 70 K). The crystal structure of YMnO$_3$ ($P\overline{6}_3cm$) can be described as stacks of corner-linked MnO$_5$ trigonal bipyramid (Mn atoms with two apical oxygen (O1 and O2) atoms and three planar oxygen (O3 and O4) atoms) layers separated by Y atom layers along the crystallographic c-axis. In the hexagonal structure there appears to be a small tilting (a cooperative tilting distortion which buckles the trigonal planes) of MnO$_5$ bipyramids, which consist of five Mn–O bonds: Mn–O1 and Mn–O2 oriented along the c direction while Mn–O3 and two pairs of Mn–O4 bonds lie within the ab plane. The noncollinear magnetic order is originating from the strong antiferromagnetic superexchange interaction of Mn spins in the ab plane of YMnO$_3$ structure below the Néel temperature $T_N$ of 70 K [2, 3]. As the symmetry breaking distortion is driven by geometric but not electronic factors in hexagonal YMnO$_3$, there is some freedom to tune the magnetic behavior of manganese atoms by electronic doping, without losing the acentric structure of host phase [4]. Doping atoms with different atomic radius will inevitably change the lattice constant and also the Mn–Mn bond distance. This change in the Mn–Mn bond distance, in particular on the ab plane, leads naturally to variations in the exchange integral, which is a critical parameter for the formation of magnetic ground state [5]. Therefore doping at the Mn site in the hexagonal YMnO$_3$, one can manipulate the physical properties and change the magnetic ground state.

In recent years, a few studies have been reported on the influence of transition metal (TM) elements doping at Mn-site in hexagonal manganite bulks [5, 6, 7, 8, 9, 10, 11, 12, 13], in which most of doping concentrations were kept about 10% to preserve the phase isostructural. For examples, N. Sharma et al. [6] pointed out that doping with 10% Ti at Mn site could reduce the temperature $T_N$ from 75 K of YMnO$_3$ compound to 55 K of polycrystalline YMn$_{0.9}$Ti$_{0.1}$O$_3$ synthesized through a solid state reaction. T. C. Han et al. [7] found that the antiferromagnetic transition temperature of YMn$_{1-x}$Cr$_x$O$_3$ ($0 \leq x \leq 0.1$) increased from 73 K to 89 K with increasing Cr-content ($x$). And F. Wan et al. [8] also reported that the $T_N$ of YMn$_{1-x}$Cr$_x$O$_3$ ($x = 0-0.1$) compounds would increase from 73.1 K to 86.1 K. S. Namdeo et al. [9] put forward that the Néel temperatures of YMn$_{1-x}$Fe$_x$O$_3$ ($0 \leq x \leq 0.1$) compounds have minutely decreased with increasing Fe- doping concentration ($x$). K. Asokan et al. [10] reported
that Co, Ni and Cu doping at Mn-site in hexagonal YMnO₃ with a specific composition of 1/3 would improve the structural and magnetic properties. L. Jeuvrey et al. [12] proposed that the magnetic transition temperature $T_N$ of hexagonal YMn₁₋ₓCuₓO₃ had decreased from 70 K down to 49 K when $x$ went from 0 to 0.15. A. M. Zhang et al. [13] revealed that the polycrystalline YMn₁₋ₓZnxO₃ with low Zn doping concentration ($x < 0.1$) maintained single phase which demonstrated hexagonal structure with space group of $P6_3cm$, and the $T_N$ temperatures were respectively 75 K, 65 K and 60 K with $x = 0, 0.04$ and 0.08.

As mentioned above, a systematic understanding of doping effect on $T_N$ is still lacking although a number of experimental results were given in TM doping YMn₀.₉₅TM₀.₀₅O₃ (TM = Ti ~ Zn) bulks. Besides, it remains to be elucidated how the antiferromagnetic interactions and Néel temperatures are modified by dopant incorporation in hexagonal manganite films [14]. In the work, we have firstly used the first-principles method to calculate a variety of TM elements from Ti to Zn atoms doping at the Mn site, and investigate how such doping affects the structural and magnetic properties of hexagonal YMn₀.₉₁₇TM₀.₀₈₃O₃ bulks (approximating to experimental YMn₀.₉TM₀.₁O₃ compositions [5, 6, 7, 8, 9, 10, 11, 12, 13]). Then we have also studied the effect of Ti, V, Cr and Fe doping on magnetic properties and discussed the varied electronic structures of TMO₅ in the YMn₀.₉₁₇TM₀.₀₈₃O₃ film configurations, which could provide more understanding towards the designing of new generation multifunctional devices.

2. Calculation

We have performed first-principles density-functional theory (DFT) calculations within the generalized gradient approximation (GGA) [15] using the Vienna ab initio Simulation Package (VASP) [16, 17]. The eigenstates of electron wave functions were expanded on a plane-wave basis set using pseudopotentials to describe the electron-ion interactions within the projector augmented-wave approach [18] (PAW). The Monkhorst-Pack (MP) scheme [19] is used for the $k$-point sampling and the Brillouin zone integration is performed with the Gaussian smearing method. The plane-wave basis energy cutoff is chosen as 500 eV. We respectively treated 11 valence electrons for Y ($4s^24p^65s^24d^1$), 15 for Mn ($3s^23p^64s^23d^5$), and 6 for oxygen ($2s^22p^4$). The atomic positions are fully relaxed until atomic forces are less than 10 meV/Å and the total energy is obtained when it converges to 0.1 meV in the electronic self-consistent loop. In the calculations, the Perdew-Burke-Ernzerhof (PBE) [15] form was chosen as the exchange-correlation potentials within the DFT + U scheme. The DFT+U integrals, determined by the PAW on-site occupancies and the on-site electron-electron interaction, are normally specified in terms of the effective on site Coulomb and exchange parameters, $U$ and $J$ [20]. Here, the values of $U = 8.0$ eV and $J = 0.88$ eV are applied for the Mn 3$d$ states [21]. $U_{eff}$ is generally
expressed as the difference between two parameters \((U-J)\), which determines an orbital-dependent correction to the DFT energy. According to the reported literatures [22, 23, 24, 25, 26, 27, 28, 29], the proper Hubbard correlation item \(U_{\text{eff}}\) values \(U_{\text{eff}}(\text{Ti}) = 3.2\, \text{eV}, U_{\text{eff}}(\text{V}) = 2.64\, \text{eV}, U_{\text{eff}}(\text{Cr}) = 3.0\, \text{eV}, U_{\text{eff}}(\text{Fe}) = 4.0\, \text{eV}, U_{\text{eff}}(\text{Co}) = 6.0\, \text{eV}, U_{\text{eff}}(\text{Ni}) = 4.7\, \text{eV}, U_{\text{eff}}(\text{Cu}) = 7.05\, \text{eV}, U_{\text{eff}}(\text{Zn}) = 8.0\, \text{eV}\) are adopted using the Dudarev implementation [30] in the following calculations. To be close to the doping concentration \(x = 0.1\) of stoichiometric component \(\text{YMn}_{1-x}\text{TM}_x\text{O}_3\) (\(\text{TM} = \text{Ti} \sim \text{Zn}\)) in the experimental reports [5, 6, 7, 8, 9, 10, 11, 12, 13], we built the supercell of a theoretical formula \(\text{YMn}_{0.917}\text{TM}_{0.083}\text{O}_3\) bulk with twelve formula units, in which one of 12 Mn atoms was substituted by a TM atom (shown in Fig. 1(a)). For each computational cell of hexagonal \(\text{YMn}_{0.917}\text{TM}_{0.083}\text{O}_3\) (\(\text{TM} = \text{Ti} \sim \text{Zn}\)) bulks (60 atoms) and the \(\text{YMn}_{0.917}\text{TM}_{0.083}\text{O}_3(001)/\text{MgO}(001)\) (\(\text{TM} = \text{Ti}, \text{V}, \text{Cr} \text{and Fe}\)) film [31] configurations (178 atoms) (shown in Fig. 1(b)), we considered three types of magnetic configurations: collinear AFM state, non-collinear magnetic \(\Gamma 1\) state and ferromagnetic (FM) state. It is found that the magnetic configurations have little effects on the optimized lattice constants. During the geometry optimizations, spin-orbit coupling (SOC) and non-collinear magnetism are regarded to calculate the energies of different magnetic configurations.

### 3. Results & discussion

#### 3.1. For the hexagonal \(\text{YMn}_{0.917}\text{TM}_{0.083}\text{O}_3\) bulks

Firstly we employed the first-principles method to calculate the lattice constants of hexagonal \(\text{YMn}_{0.917}\text{TM}_{0.083}\text{O}_3\) (\(\text{TM} = \text{Ti} \sim \text{Zn}\)) bulks. Table 1 lists the calculated

![Fig. 1](https://example.com/fig1.png)  
**Fig. 1.** Schematic of the computational cell considered for (a) the hexagonal \(\text{YMn}_{0.917}\text{TM}_{0.083}\text{O}_3\) (\(\text{TM} = \text{Ti} \sim \text{Zn}\)) bulk and (b) the \(\text{YMn}_{0.917}\text{TM}_{0.083}\text{O}_3(001)/\text{MgO}(001)\) (\(\text{TM} = \text{Ti}, \text{V}, \text{Cr} \text{and Fe}\)) film configurations, where pine green, purple, red and orange spheres indicate Y, Mn, O and Mg atoms, respectively. On the MnO layer, each Mn atom is surrounded by bipyramidal oxygen atoms which form a MnO₅ trigonal bipyramid (light yellow). The Mn atom in the green bipyramid will be substituted by a TM atom in the work.
lattice constants for the YMn$_{0.917}$TM$_{0.083}$O$_3$ compared to the earlier experimental values of bulk hexagonal YMn$_{0.9}$TM$_{0.1}$O$_3$ (TM = Ti ~ Zn). It can be seen that the lattice parameter differences between the calculated and experimental data are less than 1.0%, although the calculated compositions YMn$_{0.917}$TM$_{0.083}$O$_3$ are slightly different from the experimental constituents YMn$_{0.9}$TM$_{0.1}$O$_3$. The calculated results are in good agreement with the experiments, which proves the reliability of our computations for the doping YMn$_{0.917}$TM$_{0.083}$O$_3$ systems (including the hexagonal YMn$_{0.917}$TM$_{0.083}$O$_3$ (TM = Ti, V, Cr and Fe) film configurations).

To study the doping effects on the magnetic properties of hexagonal YMn$_{0.917}$TM$_{0.083}$O$_3$ (TM = Ti ~ Zn) bulks, the theoretical magnetic transition temperatures ($T_N$) have been calculated based on the different magnetic structures (such as collinear AFM state, non-collinear magnetic Γ1 state and FM state) and the nearest-neighbor spin-exchange interactions [36]. In all doping systems, the lowest energy state is the Γ1 state, whose lattice parameters are listed in Table 1. The calculated Néel temperatures are also listed. The formula to calculate Néel temperatures will be shown in Section 3.2. Fig. 2 shows that the calculated Néel temperatures varied with doping elements (TM) in the YMn$_{0.917}$TM$_{0.083}$O$_3$ bulks, and compared with the reported experimental values of YMn$_{0.9}$TM$_{0.1}$O$_3$ (TM = Ti ~ Zn). It can be seen that the calculated $T_N$ results clearly depend on doping elements, which agree well with those obtained from experiments. These confirm the sensitivity of magnetic properties to slight perturbations for the hexagonal YMnO$_3$ systems. And it is noteworthy that the Cr doping would induce a Néel temperature ($T_N$) increase higher than the others TM substitutions in the YMn$_{0.917}$TM$_{0.083}$O$_3$ bulks.

Table 1. Calculated lattice constants and Néel temperatures for the YMn$_{0.917}$TM$_{0.083}$O$_3$ compositions compared to experimental values of hexagonal YMn$_{0.9}$TM$_{0.1}$O$_3$ (TM = Ti ~ Zn) bulks.

| TM  | Experimental data | Calculated values |
|-----|-------------------|-------------------|
|     | $(a, c)$ (Å)      | Volume (Å$^3$)    | $T_N$ (K) |
| Ti  | 6.141, 11.370     | 371.35 [6]        | 55 [6]   |
|     |                   | 6.175, 11.535     | 380.89   | 47      |
| V   | 6.143, 11.415     | 373.04 [34]       | 89 [7], 86 [8] |
|     |                   | 6.131, 11.433     | 372.16   | 63      |
| Cr  | 6.120, 11.400     | 369.93 [35]       | 73 [7], 75 [35] |
|     |                   | 6.202, 11.539     | 384.37   | 99      |
| Mn  | 6.136, 11.429     | 372.64 [6]        | 60 [6], 67 [9] |
|     |                   | 6.163, 11.460     | 376.95   | 62      |
| Fe  |                   |                   |         |
| Co  |                   |                   |         |
| Ni  | 42 [11]           |                    |         |
| Cu  | 6.152, 11.382     | 373.05 [11]       | 59 [12] |
|     |                   | 6.198, 11.562     | 384.63   | 64      |
| Zn  | 6.179, 11.410     | 377.25 [12]       | 70 [5], 60 [13] |
|     |                   | 6.225, 11.458     | 384.50   | 67      |

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As is well known, the structural parameters can be varied by suitable substitution and hence one can tune the magnetic property in these types of materials [39]. In the YMn$_{0.917}$TM$_{0.083}$O$_3$ compounds, doping at Mn-site would cause the structural distortion of TMO$_5$ bipyramid, the magnetic ordering could be driven by the spin-exchange interaction, and the magnetic interaction strength might depend on the bond length and bond angle. Fig. 3 shows that bond length sums {\((\text{TM-O1)} + (\text{TM-O2)}, \text{ and } (\text{TM-O3)} + (\text{TM-O4})\)} and bond length ratios {\((\text{TM-O1)}/(\text{TM-O2)}, \text{ and } (\text{TM-O3)}/(\text{TM-O4})\)} change with doping elements (TM) for TMO$_3$ bipyramids in the hexagonal YMn$_{0.917}$TM$_{0.083}$O$_3$ bulks. The inset of Fig. 3 displays the TMO$_5$ bipyramid structure in which the TM atom is located at the center. It is noted in Fig. 3 that the apical bond length sum \{(TM-O1) + (TM-O2)\} are always smaller than the planar bond length sum \{(TM-O3) + (TM-O4)\}, which indicates that TM doping
would not change the basic structural characteristics of TMO$_5$ bipyramids. It is also noted in Fig. 3 that the bond length ratios \{(TM-O1)/(TM-O2), and (TM-O3)/(TM-O4)\} are almost same (around the value of 1.0). However, the ratio value of (TM-O1) to (TM-O2) has a notable deviation when Cr is the doping element. This might be one reason why the Néel temperature of YMn$_{0.917}$Cr$_{0.083}$O$_3$ exhibits an increase higher than the others YMn$_{0.917}$TM$_{0.083}$O$_3$ bulks in Fig. 2.

To further investigate the structural variations of TMO$_5$ bipyramids (shown in the inset of Fig. 3), Figs. 4 and 5 respectively demonstrate the bond lengths and bond angles dependence on doping elements (TM) from Ti to Zn. Table 2 lists the calculated main bond lengths and bond angles for TMO$_5$ bipyramid in YMn$_{0.917}$TM$_{0.083}$O$_3$ bulks, compared to available experimental values in YMn$_{0.9}$TM$_{0.1}$O$_3$ (TM = Ti, Mn and Fe) from the previous report [6], which have once again proven that our calculated results are in good agreement with the experimental ones. In Figs. 4 and 5, main bond lengths and bond angles (two structural features) of TMO$_5$ bipyramids are respectively changed with different doping elements. It is noteworthy that the variations of TM-O1 distances show a sudden rise when the bond length is Cr-O1 (in Fig. 4), meanwhile the fluctuating curves of O4-TM-O4 angles exhibit a biggest drop at O4-Cr-O4 angle (in Fig. 5), both of which suggest a significant structural distortion occurred in the CrO$_5$ bipyramid.

When compared between the CrO$_5$ and the MnO$_5$ bipyramid structures, it is clear in Fig. 3 that the planar bond length sum \{(Cr-O3) + (Cr-O4)\} is less than the \{(Mn-O3) + (Mn-O4)\} distance, but the apical bond length sum \{(Cr-O1) + (Cr-O2)\} is larger than the \{(Mn-O1) + (Mn-O2)\} distance. As results, the lengthening Cr-O1 distance would decrease the exchange interactions along the [001] direction, and the reduced O4-Cr-O4 angle would cause the bonding strength increase on the Cr-O plane. That is to say, the significant changes of two structural features of CrO$_5$.

![Fig. 4. Main bond lengths for TMO$_5$ bipyramids in hexagonal YMn$_{0.917}$TM$_{0.083}$O$_3$ bulks dependence on doping elements (TM) from Ti to Zn.](https://doi.org/10.1016/j.heliyon.2018.e00993)
bipyramid would increase the exchange interactions of planar Cr-O bonds and result in a more stable magnetic state, and eventually change the structural and magnetic properties in the hexagonal YMn$_{0.917}$Cr$_{0.083}$O$_3$ bulk system (inducing the highest $T_N$ peak as shown in Fig. 2).

3.2. For the YMn$_{0.917}$TM$_{0.083}$O$_3$(001)/MgO(001) film configurations

By performing DFT calculations, we have also examined variations of electronic structures and magnetic properties of hexagonal YMn$_{0.917}$TM$_{0.083}$O$_3$(001)/MgO(001) (TM = Ti, V, Cr and Fe) film configurations. Based on the different Néel spin states (collinear AFM state, non-collinear magnetic $\Gamma$1 state and FM state) and the nearest-neighbor spin-exchange interactions, the theoretical magnetic parameters such as transition temperatures ($T_N$) and Curie-Weiss temperatures...
(\(\Theta_{CW}\)) have been calculated [36, 37, 38] to study the doping effects of Ti, V, Cr and Fe atom at Mn site on magnetic properties of YMn\(_{0.917}\)TM\(_{0.083}\)O\(_3\)(001)/MgO(001) configurations. The nearest-neighbor spin-exchange coupling \(J_{nn}\) in the hexagonal structure of YMnO\(_3\) can be calculated as: [36]

\[
J_{nn} = \frac{1}{36(\sqrt{3} + 2)}(E_{\Gamma_1} - E_{AFM}) + \frac{1}{216}(E_{AFM} - E_{FM})
\]

where \(E_{AFM}\), \(E_{\Gamma_1}\) and \(E_{FM}\) are respectively total energies for different magnetic configurations (three Néel spin states) as collinear AFM state, non-collinear magnetic \(\Gamma_1\) state and FM state. Then according to L. Capriotti et al. [37, 38], the magnetic transition temperature can be estimated as \(T_N = -0.3J_{nn}(S + \frac{1}{2})^2\) using the nearest-neighbor spin-exchange coupling \(J_{nn}\) and the absolute value of Mn spin \(S\). The theoretical Curie-Weiss temperature can be calculated using the expression: \(\Theta_{CW} = \left(\frac{1}{3}\right) \cdot Z \cdot J_{nn} \cdot S \cdot (S + 1)\) [36], where Z is the number of nearest neighbors.

Table 3 lists the calculated values of magnetic parameters of YMn\(_{0.917}\)TM\(_{0.083}\)O\(_3\)(001)/MgO(001) (TM = Ti, V, Cr and Fe) configurations. It can be found that Cr doping would also induce a \(T_N\) increase of film configuration similar to the YMn\(_{0.917}\)Cr\(_{0.083}\)O\(_3\) bulk, however, others doping (Ti, V and Fe) would make Néel temperatures reduced to some degree. As we know, the antiferromagnetic ordering temperature of YMnO\(_3\) is much lower than the absolute value of the Curie-Weiss temperature. Due to the antiferromagnetic interactions, the Curie-Weiss temperatures are negative in the film configurations. It is noted that the variation trends of absolute value of Curie-Weiss temperature \(|\Theta_{CW}|\) are consistent with the Néel temperatures. With the doping elements (Ti, V, Cr and Fe), the calculated effective magnetic moments (\(\mu_{\text{eff}}\)) have decreased slightly when compared to pure YMnO\(_3\)(001)/

Table 3. Calculated values of magnetic parameters of YMn\(_{0.917}\)TM\(_{0.083}\)O\(_3\)(001)/MgO(001) (TM = Ti, V, Cr and Fe) configurations. \(\Delta T_N\) is a difference between the Néel temperature of a doped compound and the pure one. The effective magnetic moment is averaged magnetic moment of TM and Mn in the doped system.

| TM   | \(T_N\) (K) | \(\Delta T_N\) (K) | \(\Theta_{CW}\) (K) | \(\mu_{\text{eff}}\) (\(\mu_B\)) | \(f\) |
|------|-------------|---------------------|---------------------|-----------------------------|------|
| Ti   | 123         | -24                 | -789                | 4.50                        | 6.415|
| V    | 121         | -26                 | -778                | 4.53                        | 6.429|
| Cr   | 161         | 14                  | -1031               | 4.62                        | 6.404|
| Mn   | 147 [31]    | 0                   | -946                | 4.70                        | 6.435|
| Fe   | 118         | -29                 | -757                | 4.61                        | 6.415|
MgO(001) configuration. Nevertheless, the $\mu_{\text{eff}}$ values of Cr, Mn and Fe doping are comparable within the difference (2%). The value of parameter $f = \frac{\Theta_{\text{CW}}}{T_N}$ is a magnetic frustration factor which can be used as a measure of the spin frustration strength. If the ratio $f$ is larger than 10, the spin system should be classified as the one with strong geometrical frustration since the value cannot be explained by the simple mean-field theory [40]. For the hexagonal YMnO$_3$ bulk, the calculated $\Theta_{\text{CW}}$ is $-468$ K and $T_N$ is $73$ K, then the frustration factor ($f = 6.41$) can be obtained; which is very close to the experimental value ($f = 6.43$) [9]. For the YMn$_{0.917}$TM$_{0.083}$O$_3$(001)/MgO(001) configurations, it can be seen in Table 3 that the $f$ parameters remain almost the same (the deviations are less than 0.5%) and seem to be independent on the doping elements (TM = Ti, V, Cr and Fe). Because the magnetic interaction strength depends on the extent of orbital overlap and the covalent bond, we next calculated the orbital-resolved density of states (DOS) for further understanding of TM doping effect on electronic structure characteristics of TMO$_5$ bipyramids in YMn$_{0.917}$TM$_{0.083}$O$_3$(001)/MgO(001) configurations.

As we know, the crystal field of hexagonal YMnO$_3$ splits the Mn $d$ orbitals into two doublets ($e_{1g}$ and $e_{2g}$) and a singlet ($a_{1g}$). In the TMO$_5$ bipyramids (shown in the inset of Fig. 3), the $d_z^2$ orbitals ($a_{1g}$) would like to point towards the apical oxygens (O1 and O2) favorable to the bonding {TM-O1}+(TM-O2), and the $d_{xy}$ and $d_{x^2-y^2}$ orbitals ($e_{2g}$) towards the planar oxygens (O3 and O4) in favor of covalent bonding {TM-O3}+(TM-O4). Fig. 6 shows the orbital-resolved DOSs of the individual TM (TM = Ti, V, Cr, Mn and Fe) $d$ for TMO$_5$ bipyramids in YMn$_{0.917}$TM$_{0.083}$O$_3$(001)/MgO(001) configurations ($d_{yz}$ and $d_{zx}$ not shown). In the energy range between $-7.6$ eV and $-3.1$ eV where O $p$ orbitals locate, the TM orbital $d_z^2$ DOS’s will be responsible for the $d_z^2$ (TM)$-p_z$ (O1 or O2) interaction, and the TM $d_{xy}$ (shaded gray in Fig. 6) and $d_{x^2-y^2}$ orbitals will be in charge of

![Fig. 6. Orbital-resolved density of states of the individual TM (TM = Ti, V, Cr, Mn and Fe) $d$ for TMO$_5$ bipyramids in YMn$_{0.917}$TM$_{0.083}$O$_3$(001)/MgO(001) configurations as a function of energy ($E-E_F$), in which $E_F$ is the Fermi energy. Solid and dashed lines denote majority and minority states, respectively.](https://doi.org/10.1016/j.heliyon.2018.e00993)
hybridization with the in-plane O3(O4) \( p_x \) and \( p_y \). Note that the occupied states of Cr \( e_{2g} (d_{xy} \) and \( d_{z^2} \)) orbitals illustrate a stronger hybridization trend with O3(O4) \( p_x \) and \( p_y \) orbitals than the other TM (Ti, V, Mn and Fe) doping’s DOS states, and the occupied states of Cr \( a_{1g} (d_{z^2}) \) orbitals exhibit a less interaction with O1(O2) \( p_z \) orbitals than the states of V and Mn orbitals (energy ranging from \(-7.6\) eV to \(-3.1\) eV), all of which suggest that the increase of orbital interactions involved in the planar Cr-O covalent bonds, and the slight decrease of apical Cr-O orbital interactions have both accounted for the increase of magnetic ordering temperature in the YMn\(_{0.917}\)Cr\(_{0.083}\)O\(_3\)(001)/MgO(001) configuration.

4. Conclusions

In conclusion, the Mn-site doping behaviors of hexagonal YMn\(_{0.917}\)TM\(_{0.083}\)O\(_3\) systems have been systematically studied by using the first-principles method. The calculated Néel temperatures, varied with doping elements in YMn\(_{0.917}\)TM\(_{0.083}\)O\(_3\) bulks, are in agreement with the reported experimental values of YMn\(_{0.9}\)TM\(_{0.1}\)O\(_3\) (TM = Ti \( \sim \) Zn). We have found that the structural changes of TMO\(_5\) bipyramids would lead to the transformations of magnetic properties. The planar TM-O bonds and O-TM-O angles of TMO\(_5\) bipyramid are both important structural features for the changes of magnetic ordering temperatures. Then the doping effects of transition metal Ti, V, Cr and Fe at Mn site have also been predicted on the varied magnetic properties of YMn\(_{0.917}\)TM\(_{0.083}\)O\(_3\)(001)/MgO(001) film configurations, in which the Cr doping would also induce a \( T_N \) increase higher than the others doping similar to the YMn\(_{0.917}\)Cr\(_{0.083}\)O\(_3\) bulk. By analyses of electronic structures, it can be found that the occupied states of TM \( e_{2g} (d_{xy} \) and \( d_{z^2} \)) and TM \( a_{1g} (d_{z^2}) \) orbitals are simultaneously responsible for the strength of covalent bonds and eventually influence on the magnetic transition temperatures. These insightful results could provide more understanding towards the transition metal doping effect on the structural, electronic and magnetic properties of YMnO\(_3\) films and the designing of new generation multifunctional devices.

Declarations

Author contribution statement

Dong Chen: Analyzed and interpreted the data, Wrote the paper.

Yu-Jia Wang: Conceived and designed the analysis.

Yin-Lian Zhu, Xiu-Liang Ma: Contributed analysis tools or data.

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**Competing interest statement**

The authors declare no conflict of interest.

**Additional information**

No additional information is available for this paper.

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