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First-Principles Study of Magnetism in Transition Metal Doped $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ System

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The origins of magnetism in transition-metal doped $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ system are investigated by *ab initio* calculations. The calculated results indicate that a transition-metal atom substitution for a Ti atom produces magnetic moments, which are due to the spin-polarization of transition-metal 3d electrons. The characteristics of exchange coupling are also calculated, which shows that in Cr-/Mn-/Fe-/Co- doped $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ system, the antiferromagnetic coupling is favorable. The results can successfully explain the experimental phenomenon that, in Mn-/Fe- doped $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ system, the ferromagnetism disappears at low temperature and the paramagnetic component becomes stronger with the increase of doping concentration of Mn/Fe/Co ions. Unexpectedly, we find the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.67}\text{V}_{0.33}\text{O}_3$ system with ferromagnetic coupling is favorable and produces a magnetic moment of $2.00 \mu_B$, which indicates that low temperature ferromagnetism materials could be made by introducing V atoms in $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$. This may be a new way to produce low temperature multiferroic materials.

Key words: Transition-metal atom, Substitution, Magnetic moment, First-principles calculation.

I. INTRODUCTION

In recent years, multiferroic materials have drawn increasing interest due to their attractive physical properties and potential applications in spintronics, information storage and sensors [1–4]. The coupling between the magnetic and electric properties could lead to magnetoelectric effect [1] in which the magnetization can be controlled by application of electric fields, and vice versa. Multiferroic properties have been found in some oxides with perovskite structure [5–7]. The observed single-phase multiferroic materials are few [8], due to the contradiction between the conventional mechanism for cation off-centering in ferroelectrics (which generally requires d^0 orbitals), and the formation of magnetic moments (which usually results from partially filled d or f orbitals). Related studies on magnetic ferroelectrics have signalled a revival of interest in this phenomenon [2]. Several reports show that doping of transition metal ions in a ferroelectric oxide could induce ferromagnetism, a similar case to that of diluted magnetic semiconductors [9, 10].

$\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ attracts much attention as a promising environmental friendly lead-free ferroelectric mate-

rial due to its possible applicability to electromechanical actuators, sensor, and transducers [11]. It is one among the non-lead free relaxor ferroelectrics having very high remanent polarization $P_r=36 \mu\text{C}/\text{cm}^2$ with a coercive field of about 70 kV/cm [12]. At temperatures below 255 °C $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ has a rhombohedral structure with R3c space group which has anti-phase ($\bar{a}\bar{a}\bar{a}$) octahedral tilting and ion displacements along the [111] direction of the pseudo-cubic cell, making $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ exhibit unique ferroelectric and piezoelectric properties [13]. In such systems inducing a multifunctional behavior by site specific substitution will be inevitable. In $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$, diluted magnetic behavior has been observed by transition-metal substitution at B-site, such as Fe-/Mn-/Co-doped $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ [14–16]. All the results above indicate that the substitutional doping with transition metals play a very important role in tuning the electronic and magnetic properties of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ and related systems. However, the mechanisms of electronic and magnetic of TM-doped $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ remain unclear.

In order to address exactly these above questions, we explore the electronic and magnetic properties of bulk of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ with transition metals doping via the first-principles density functional theory (DFT). Results demonstrate that, for $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ system,

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magnetic moments can be induced when one Ti atom is substituted by a TM (TM=V, Cr, Mn, Fe, and Co) atom. We also compared the energies of ferromagnetic and antiferromagnetic couplings between two TM atoms substitutions in $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ super-cell. The type of preferential magnetic coupling of system depends upon both the doped transition-metal atoms and the distributions of the Ti atoms substituted. The TM doping concentration was defined as the molar ratio of TM/(TM+Ti).

II. COMPUTATIONAL DETAILS

DFT calculations were performed using the plane-wave pseudopotential method in the Vienna *ab initio* simulation package (VASP) [17, 18]. The projector augmented wave (PAW) [19, 20] potentials were employed. Considering the fact that LDA may underestimate the Coulomb repulsion and tend to localize the charge density, strong correlation effects were introduced by means of the LDA+ U scheme [19]. In our LDA+ U calculation, the on-site effective U parameter ($U_{\text{eff}}=U-J=5.8$ eV) was proposed by Dudarev *et al.* [21]. The calculated lattice constants of ($a=b=5.49$ Å, $c=13.51$ Å, and $\alpha=\beta=90^\circ$, $\gamma=120^\circ$) are in good agreement with reported results by Jones and Thomas [13]. Special k points were generated with a $3\times 3\times 3$ grid based on Monkhorst-Pack scheme. We constructed a rhombohedral $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ periodic supercell containing 30 atoms, where a Ti atom is substituted by a TM atom (TM=V, Cr, Mn, Fe, and Co). Such substitution corresponds to $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.84}\text{V}_{0.16}\text{O}_3$ and the doping level is 16%. An energy cutoff of 400 eV was used for the plane wave expansion of the electronic wave function. The cases of pure $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ and TM atoms (TM=V, Cr, Mn, Fe, and Co) doped $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ are considered. The total energy is converged to be 1.0×10^{-4} eV/atom, while the Hellman-Feynman force is smaller than 0.01 eV/Å in the optimized structure.

III. RESULTS AND DISCUSSION

The rhombohedral $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$, a complex perovskite-structure compound with Na and Bi ions at the A site of ABO_3 with a Na:Bi ratio of 1:1 are shown in Fig.1. The density of state (DOS) for the pure system $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ is given in Fig.2(a). In addition, the total DOS for pure $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ system also shows that no spin-polarization emerges around the Fermi energy level, indicating that the pure $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ is nonmagnetic, as there are no unpaired electrons, the results are in good agreement with Zhang's report [22].

Experimental evidence has shown that the transition-metal atoms replace the Ti atoms at B-site [14, 15]. Calculations have been performed on $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.84}\text{V}_{0.16}\text{O}_3$ (TM=V, Cr, Mn, Fe and Co).

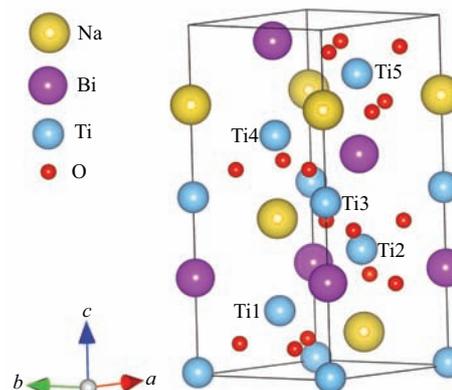


FIG. 1 The schematic crystal structure of rhombohedral $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$.

The total DOSs of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.84}\text{V}_{0.16}\text{O}_3$ (TM=V, Cr, Mn, Fe, and Co) are shown in Fig.2 (b)–(f). An obvious spin-split in the spin-up and spin-down total DOS at/near the Fermi level can be found. Clearly, V-, Cr-, Fe-, and Co-doped $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ are all half-metals and magnetic with 100% spin polarization. The Mn-doped $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ is magnetic semiconductor, because both the majority and minority spin DOSs are zero at the Fermi level and there is a clear spin polarization between the DOSs of the two spin channels around the Fermi level. According to our calculations, the values of magnetic moments are 1.00, 2.00, 3.00, 2.00, and 1.01 μ_B for 16% V-, Cr-, Mn-, Fe-, and Co- doped $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$, respectively. The total energies of the supercell with $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.84}\text{TM}_{0.16}\text{O}_3$ (TM=V, Cr, Mn, Fe and Co) for spin-polarized and nonspin-polarized modes are also calculated. The corresponding energy difference $\Delta E_{N-M}=E_N-E_M$ between the total energies of nonmagnetic state E_N and the magnetic state E_M are 0.12, 0.64, 1.32, 0.47 and 0.07 eV for 16% V-, Cr-, Mn-, Fe-, and Co-doped $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$, respectively. All the results show that the magnetic state is more stable than the nonmagnetic one. Figure 3 (a)–(e) show the spin-density distribution (spin-up minus spin-down) for $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.84}\text{TM}_{0.16}\text{O}_3$ (TM=V, Cr, Mn, Fe, and Co). The spin density is mainly distributed on the TM atoms.

In order to further understand the electronic structure, the atom-, orbital-, and spin-projected density of the TM atom (TM=V, Cr, Fe and Co) d states, Na atoms s, p states, Bi atoms s, p, d states, Ti s, p, d states, and O p states are calculated and presented in Fig.4 for V-, Cr-, Fe-, and Co-doped $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$. Obviously, the TM 3d DOS shows an exchange splitting between the spin-up and spin-down DOS peaks at/near the Fermi level, which results in a magnetic moment. As shown in Fig.3 (c)–(e), small induced magnetic moments are also observed for the O atoms. The difference between the spin-up and spin-down DOS of O p

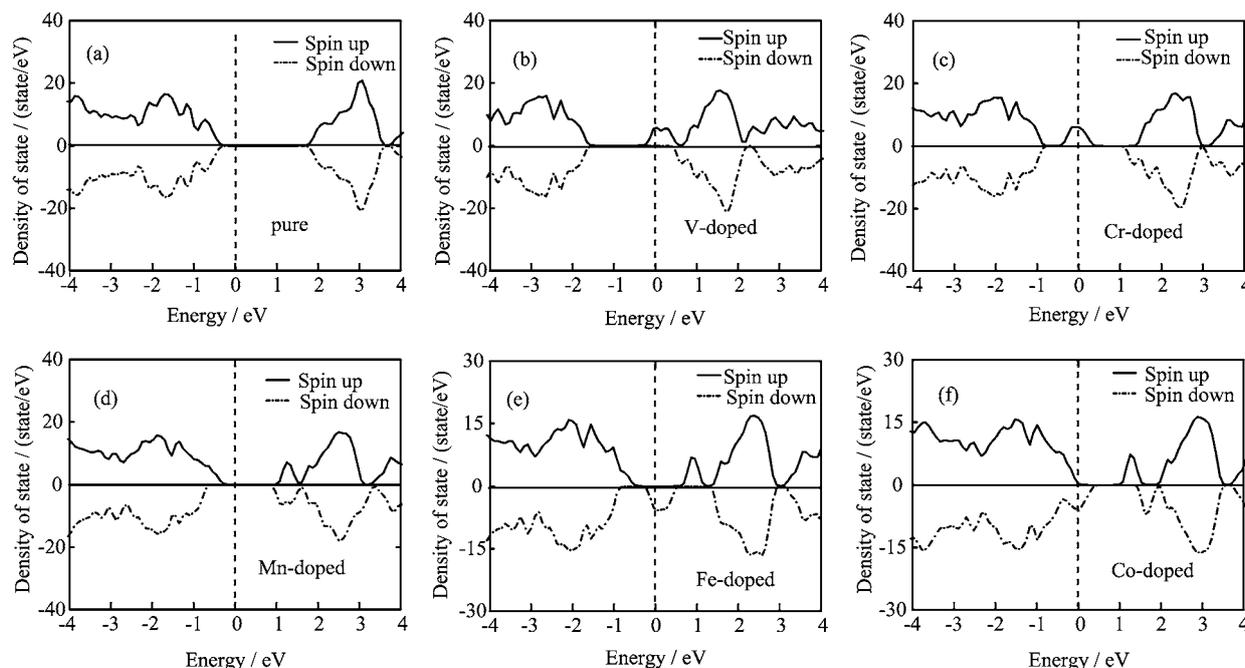


FIG. 2 Total density of state of (a) pure $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$, (b) $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.84}\text{V}_{0.16}\text{O}_3$, (c) $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.84}\text{Cr}_{0.16}\text{O}_3$, (d) $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.84}\text{Mn}_{0.16}\text{O}_3$, (e) $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.84}\text{Fe}_{0.16}\text{O}_3$ and (f) $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.84}\text{Co}_{0.16}\text{O}_3$, respectively. The vertical dotted line indicates the Fermi level.

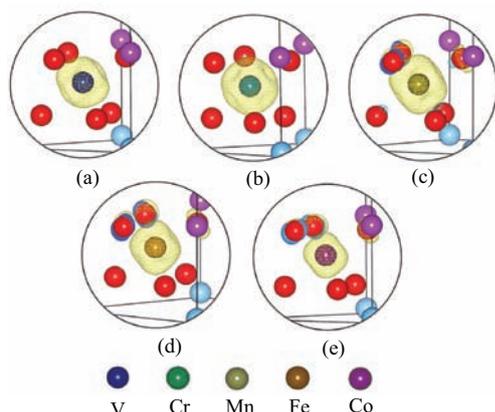


FIG. 3 Three-dimensional iso-surfaces of magnetization density for (a) $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.84}\text{V}_{0.16}\text{O}_3$, (b) $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.84}\text{Cr}_{0.16}\text{O}_3$, (c) $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.84}\text{Mn}_{0.16}\text{O}_3$, (d) $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.84}\text{Fe}_{0.16}\text{O}_3$, and (e) $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.84}\text{Co}_{0.16}\text{O}_3$. The yellow iso-surfaces represent the spin density of spin up. The iso-value is $0.01 \text{ e}/\text{\AA}^3$.

states can be found, which can be seen in Fig. 4 (a)–(d). The O atoms around the 3d TM atoms are polarized while other O atoms are not. That is to say, the polarized electrons are decided by the distance between the O atom and the TM atom. The spin-projected DOS of spin-up orbitals (or spin-down orbitals) pass through the Fermi level and spin-down orbitals (or spin-up orbitals) can exhibit the characteristics of semiconductor. Therefore, V-, Cr-, Fe-, and Co-doped $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$

TABLE I Distance between two Ti atoms substituted by TM (TM=V, Cr, Mn, Fe, and Co) for the three cases of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.67}\text{TM}_{0.33}\text{O}_3$.

Case	$\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.67}\text{TM}_{0.33}\text{O}_3$				
	V	Cr	Mn	Fe	Co
Ti1 and Ti2	3.76	3.77	3.79	3.73	3.73
Ti1 and Ti3	5.42	5.40	5.39	5.35	5.34
Ti1 and Ti4	6.71	6.69	6.67	6.63	6.64

are the half-metal materials.

Subsequently, we perform spin polarized calculations on the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ supercell with two TM (TM=V, Cr, Mn, Fe and Co) atoms substituting for Ti atoms in the lattice. Such substitution corresponds to $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.67}\text{TM}_{0.33}\text{O}_3$ and the doping level is 33%. In the supercell, we investigate three distributions of the two Ti atoms, which are replaced by TM atoms. The three cases are: (i) the two TM atoms are located at the sites of Ti1 and Ti2, respectively, (ii) the two TM atoms are located at the sites of Ti1 and Ti3, respectively, (iii) the two TM atoms are located at the sites of Ti1 and Ti4, respectively. The value of the distance between the two TM atoms located at the sites of Ti1 and Ti5 is too large (more than 9 \AA), and the magnetic coupling effect is very weak. Therefore, the case of two TM atoms located at the sites of Ti1 and Ti5 is not meaningful to discuss here.

After absolutely optimized, as shown in Table I, the distances between TM (TM=V, Cr, Mn, Fe, and Co)

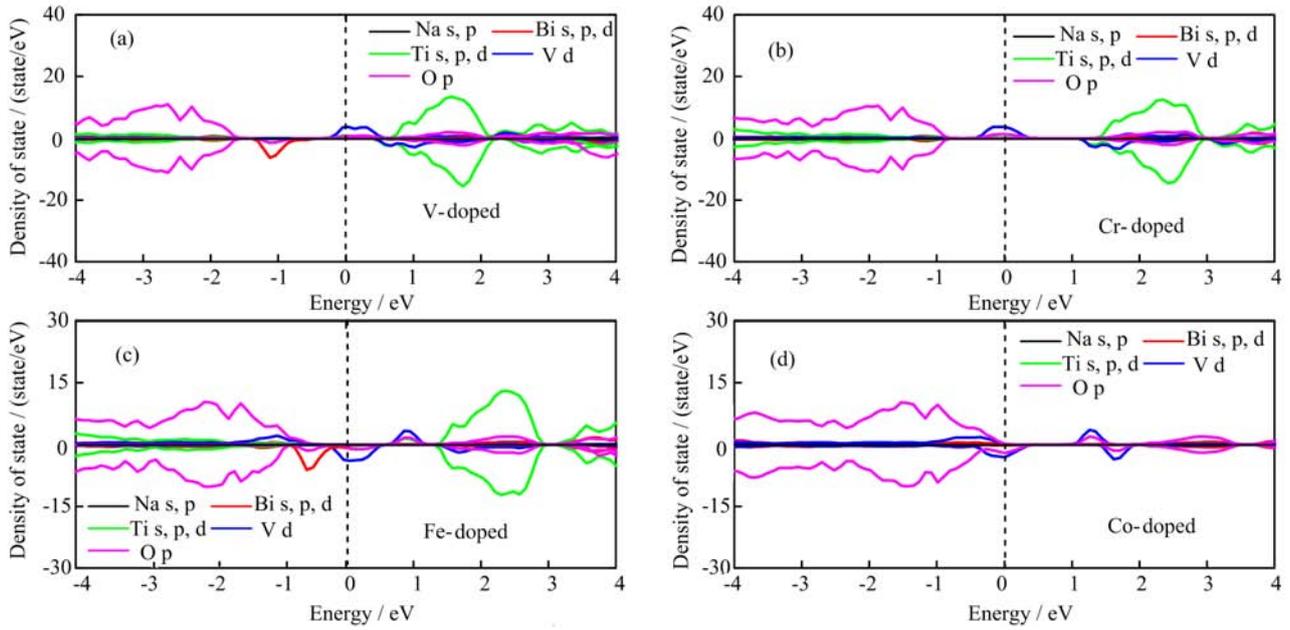


FIG. 4 Partial DOS of TM d states, Na s, p states, Bi s, p, d states, Ti s, p, d states, V d states, and O p states for $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.84}\text{TM}_{0.16}\text{O}_3$ and TM=(a) V, (b) Cr, (c) Fe and (d) Co, respectively. The vertical dotted line indicates the Fermi level.

TABLE II The relative energies of the states FM and AFM ($\Delta E_m = E_{\text{AFM}} - E_{\text{FM}}$), values of the relative stabilities ΔE , calculated for the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.67}\text{TM}_{0.33}\text{O}_3$ (TM=V, Cr, Mn, Fe, and Co).

Case	$\Delta E_m/\text{meV}$					$\Delta E/\text{meV}$				
	V	Cr	Mn	Fe	Co	V	Cr	Mn	Fe	Co
Ti1 and Ti2	173.13	-382.16	-15.86	-30.88	-14.80	0	15.07	158.68	0	0
Ti1 and Ti3	65.07	-1375.12	-26.97	-80.56	-10.54	195.49	0	0	388.48	14.62
Ti1 and Ti4	36.70	-1441.12	-7.04	-124.30	-5.43	315.62	51.80	56.46	182.66	74.6

atoms for the three cases are almost the same. In order to deal with the effect of the magnetic coupling between the two isolated TM atoms, we evaluate the relative energies between ferro- and antiferromagnetically ordered states by LDA+ U calculation. Table II provides the energy differences between ferromagnetic state (FM) and antiferromagnetic state (AFM) as well as magnetic moments of two TM atoms doping. Here, $\Delta E_m = E_{\text{AFM}} - E_{\text{FM}}$ represents energy difference between antiferromagnetic state and ferromagnetic state after optimization, which enables us to estimate stable states of magnetism coupling. $\Delta E_m > 0$ indicates that the ferromagnetic state is more stable than the antiferromagnetic state, while $\Delta E_m < 0$ indicates that the antiferromagnetic state is more stable than the ferromagnetic state. The energy differences ΔE of structures with different distance between the two TM atoms substitution for Ti atoms in $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ are also listed in Table II. By comparing the total energies of the above three cases for $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.67}\text{TM}_{0.33}\text{O}_3$ (TM=V, Cr, Mn, Fe, and Co), we find that the type of preferential magnetic coupling of system depends upon both the doped transition-metal atoms and the distributions of

the Ti atoms substituted.

For the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.67}\text{TM}_{0.33}\text{O}_3$ (TM= Fe and Co) system, when the two Fe/Co atoms are located at the sites of Ti1 and Ti2, the system with antiferromagnetic coupling has the lowest energy among the three cases; For the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.67}\text{TM}_{0.33}\text{O}_3$ (TM=Cr and Mn) system, when the two Cr/Mn atoms are located at the sites of Ti1 and Ti3, the system with antiferromagnetic coupling has the lowest energy among the three cases. Wang *et al.* reported experimentally that, as Mn ions doping concentration was increased to 20%, the Mn-doped $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ sample shows a strong ferromagnetism at room temperature. However, with further increasing the doping concentration of Mn ions up to 30%, the paramagnetic component becomes stronger [15]. Duan *et al.* found the ferromagnetism disappeared at 10 K and indicated that inside the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{1-x}\text{Mn}_x\text{O}_3$ particles, the antiferromagnetic coupling between the Mn ions can be formed [23], which conformed our calculation results. For the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.67}\text{V}_{0.33}\text{O}_3$ system, when the two V atoms are located at the sites of Ti1 and Ti2, the system with ferromagnetic coupling has the lowest energy among the three cases and produces a

magnetic moment of $2.00 \mu_B$, indicating that low temperature ferromagnetism materials could be made by introducing V atoms in $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$. This may be a new way to produce multiferroic materials.

IV. CONCLUSION

We explore the structural, electronic and magnetic properties of TM-doped (TM=V, Cr, Mn, Fe and Co) $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ alloys via the first-principles PAW potential within DFT, employing the exchange-correlation potential provided by the LDA+*U*. The results demonstrate that, for $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ system, magnetic moments can be induced when one Ti atom is substituted by a TM atom. On the electronic structures, the analyses of total DOSs indicate that V-, Cr-, Fe- and Co- doped $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ alloys are all half-metals and magnetic with 100% spin polarization. It also can be found that the magnetic phase is energetically preferred to the nonmagnetic phase for all the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.84}\text{TM}_{0.16}\text{O}_3$ (TM=V, Cr, Mn, Fe and Co) systems. For V-, Cr-, Fe- and Co- doped $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ alloys, the results of spin-projected DOS show that the spin splitting mainly comes from TM3d states. Small magnetic moments are also observed for the O atoms, which are due to the small spin polarization of p-states of O atoms. We also compared the energies of ferromagnetic and antiferromagnetic couplings between two TM (TM=V, Cr, Mn, Fe and Co) atoms substitutions in $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ supercell, in which we investigate three distributions. For Cr-/Mn-/Fe-/Co-doped $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ system, antiferromagnetic coupling is more stable. The results can successfully explain the experimental phenomenon that, in Mn/Fe doped $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ system, the ferromagnetism disappears at low temperature and the paramagnetic component becomes stronger with the increase of doping concentration of Mn/Fe/Co ions. Furthermore, we find the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.67}\text{V}_{0.33}\text{O}_3$ system with ferromagnetic coupling is favorable and produces a magnetic moment of $2.00 \mu_B$, which indicating that low temperature ferromagnetism materials could be made by introducing V atoms in $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$. This may be a new way to produce low temperature multiferroic materials.

V. ACKNOWLEDGMENTS

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