First-principles Research on New Half-metallic ferromagnets: NaCl-type TM-doped CaO

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Abstract

New half-metallic ferromagnets $Ca_{0.75}TM_{0.25}O$ (TM=V, Cr and Mn) are predicted, and then their structural, electric and magnetic properties are investigated by performing first-principles calculations within the generalized gradient approximation for the exchange-correlation function based on density functional theory. The total energy calculation shows that TM-doping can induce the stable ferromagnetic state and the stable half-metallicity in CaO with NaCl structures. Their spin-polarization at the Fermi level is all absolutely +100%. Supercell magnetic moments of $Ca_{0.75}V_{0.25}O$, $Ca_{0.75}Cr_{0.25}O$ and $Ca_{0.75}Mn_{0.25}O$ are 3.00, 4.00 and 5.00 μ_B, respectively. Their magnetism, conductance and half-metallicity come mainly from the spin-polarization of TM 3d-orbitals caused by strong octahedral crystal field in the ligand compound ML_6 consisting of the TM ion and O ligands around it. The electronic structures of TM-ions are V $t_{2g}^{3}\uparrow$, Cr $t_{2g}^{3}\uparrow e_g^{1}\uparrow$ and Mn $t_{2g}^{3}\uparrow e_g^{2}\uparrow$, respectively.

Keywords

Half-metallicity, electric and magnetic properties, crystal cell magnetic moments.

1. Introduction

Spintronics, the potential second-generation electronics, focuses on the transmission of both charges and spins of electrons. Spintronic devices have many advantages such as nonvolatility, increased data processing speed, decreased electric power consumption, and increased integration densities compared with conventional semiconductor devices only considering the transmission of charges [1-3]. Therefore, there is increasing interest on the spintronic materials, especially the half metallic ferromagnets (HMFs) whose spin-polarization at the Fermi level (E_f) is theoretically ±100% [1-3]. Compared with ordinary magnetic materials, HMFs have higher spin-polarization at E_f, and then possibly higher magnetoresistance effect, which is very important in designing spintronic devices. Furthermore, realization of spintronic semiconductor devices requires highly spin-polarized current injected from magnetic electrodes. HMFs have complete spin-polarization, and their resistivity matches well with semiconductors, so they are considered as best magnetic electrode materials.

Many HMFs had been predicted theoretically or prepared experimentally [4-11]. Recently, more and more interesting have been caused on alkaline-earth Oxides or sulfides with NaCl structures. The main reason is that these HMFs possibly have high Curie temperatures and stable physical properties including the half-metallicity, and then wide important application in spintronic devices. Elfimov et al reported that Ca vacancies in CaO lead to half-metallic ferromagnetic ground state [12]. We had predicted X4CY3 compounds (X = Mg, Ca, and Sr and Y = O and S) with NaCl structure as half-metallic ferromagnets using pseudo-potential method [7]. C- or N-doped CaO, SrO, MgO, BaO and alkaline-earth sulfides were also found as HMFs [13-17]. Yogeswari et al found that (N, P, As and Sb) doped alkaline-earth sulfides are also HMFs [18]. Some HMFs had been confirmed by experimental observation, for an example as the N-doped MgO [19]. These outstanding achievements are very important to the development of theoretic and experimental studies of spintronics. However, there are a few problems for this class of HMFs, namely, their Curie temperatures are not high enough and their half-metallicity are not stable enough. Therefore their application is restricted in spintronics. In this paper, some new HMFs with high Curie temperatures and stable half-metallicity, namely (V, Cr and Mn)-doped CaO, are predicted and their structural, electric and magnetic properties are investigated in detail based on density functional theory.

2. Model and calculation method

In order to achieve the realistic experimental dopant concentration (5-30%), a periodic 4×4 supercell consisting of four Ca-ions and four O-ions is selected as the substrate. Then the Ca-ion on the center of the supercell is replaced by one X-ion (X=V, Cr and Mn), so the dopant concentration is 25.0 %. The doped supercell Ca0.75X0.25O is shown in Fig. 1, where blue, green and red spheres represent the X, Ca and O-ions, respectively. The space group is Fm-3m. The optimization of geometrical structures and the calculation of magnetic and electric properties are performed using the calculation module ′castep′ based on the density functional theory. The wave functions are expanded with the plane-wave pseudopotentials, and the exchange correlation functions are the Perdew–Burke–Ernzerhof functional of three nonlocal gradient corrected exchange-correlation functionals (GGA), which have been widely used for the optimization of structures and the calculation of magnetic and electric properties of new materials recently [20-23]. The calculation quality is elected as ′fine′, corresponding to the cutoff energy 430 eV and the k-point set 5×5×5. The calculated electronic structures of corresponding isolated atoms are 3s23p63d34s2, 3s23p63d54s1, 3s23p63d54s2, 3s23p64s2 and 2s22p4 for V, Cr, Mn, Ca and O-atom, respectively.

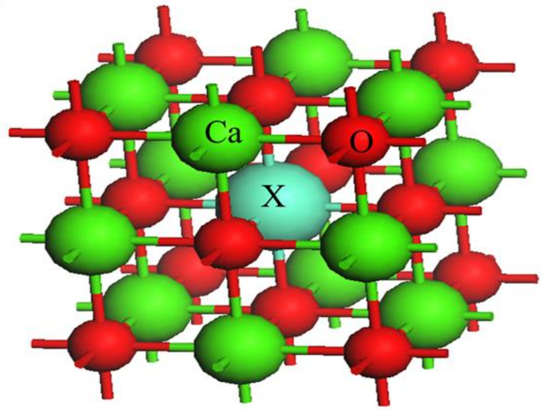


Fig.1 The Ca3XO4 supercell (X=V, Cr and Mn)

3. Results and discussions

3.1 Total state densities of $Ca_{0.75}TM_{0.25}O$

Total spin-polarized densities of states (TDOS) of $Ca_{0.75}TM_{0.25}O$ (TM=Ti, V, Cr and Mn) are shown in Fig.2, where the solid and dashed lines show the TDOS of up-spin and down-spin sub-bands, respectively. From Fig.2, the spin polarization of $Ca_{0.75}V_{0.25}O$, $Ca_{0.75}Cr_{0.25}O$ and $Ca_{0.75}Mn_{0.25}O$ at the Fermi energy (E_f) is absolutely +100% so that they are really HMFs. However, for $Ca_{0.75}Ti_{0.25}O$, the up-spin and down-spin TDOS at E_f are equal to each other, so $Ca_{0.75}Ti_{0.25}O$ is not a HMF. Especially, there is no magnetism induced by Ti-doping in CaO. $Ca_{0.75}TM_{0.25}O$ (TM=Ti, V, Cr and Mn) have similar up-spin and down-spin TDOS below -8 eV, which are axisymmetric about the energy-axis. They cause no influence on electronic and magnetic properties of $Ca_{0.75}TM_{0.25}O$, so they are not plotted here due to limited space. The main reason is perhaps that Ti, V, Cr and Mn have similar atomic orbit structures. If their energy is far lower than the Fermi level, their orbits will be not influenced by the crystal field. In fact, the central TM-ion and its six ligands O-ions form the ligand compound ML_6, and then the strong Coulomb interaction, namely the octahedral crystal field, is caused in the ML_6. However, TDOS of $Ca_{0.75}TM_{0.25}O$ near the Fermi level are evidently different with each other. This shows that the octahedral crystal field is very strong and is relative to the number of electrons in the ML_6. Their Fermi levels relatively move toward lower energy when the dopants vary from Ti to Mn. The main reason is perhaps that intra-ionic interactions including Coulomb repulsion and exchange interaction are stronger if these supercells have more electrons. $Ca_{0.75}V_{0.25}O$, $Ca_{0.75}Cr_{0.25}O$ and $Ca_{0.75}Mn_{0.25}O$ have more electrons than $Ca_{0.75}Ti_{0.25}O$ evidently. Stronger intra-atomic interaction results in larger separation of their down-spin sub-bands and pushes the Fermi levels toward the lower energy.

From Fig.2, the spin gap 2.96 eV of $Ca_{0.75}V_{0.25}O$, defined as the energy distance from the maximum energy of down-spin valence sub-bands to the minimum energy of the down-spin conduction sub-bands, is a little lower than 3.10 eV of $Ca_{0.75}Cr_{0.25}O$. However it is evidently higher than 2.43 eV of $Ca_{0.75}Mn_{0.25}O$. The spin-flip gaps or half-metallic gaps, defined as the smaller energy distance from the Fermi level of the metallic sub-bands to the top of semiconductor valence sub-bands and the bottom of semiconductor conduction sub-bands, are 1.04 eV,1.31 eV, 1.14 eV for $Ca_{0.75}V_{0.25}O$, $Ca_{0.75}Cr_{0.25}O$ and $Ca_{0.75}Mn_{0.25}O$, respectively. The spin-flip gaps are often used to indicate the half-metallic stability of HMFs. This shows that the half-metallicity of $Ca_{0.75}Cr_{0.25}O$ is evidently more stable than $Ca_{0.75}V_{0.25}O$ and $Ca_{0.75}Mn_{0.25}O$. On the other hand, the up-spin TDOS (2.75 electrons/eV) of $Ca_{0.75}V_{0.25}O$ is much larger than $Ca_{0.75}Cr_{0.25}O$ (1.26 electrons/eV) and $Ca_{0.75}Mn_{0.25}O$ (1.19 electrons/eV) at the Fermi level. This shows that the conductivity of $Ca_{0.75}V_{0.25}O$ is much higher than that of $Ca_{0.75}Cr_{0.25}O$ and $Ca_{0.75}Mn_{0.25}O$.

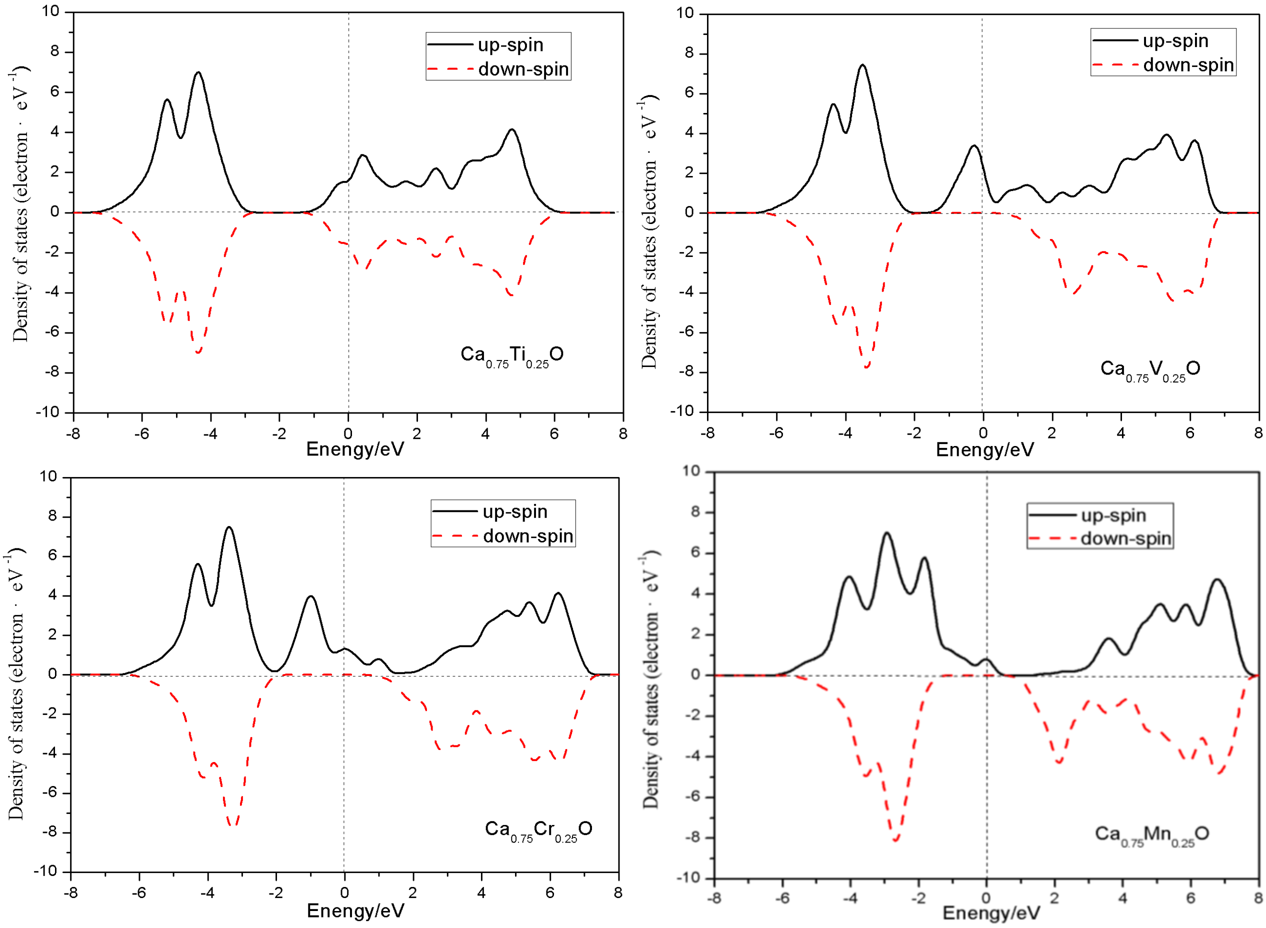


Fig.2 Spin-polarized total state densities of $Ca_{0.75}TM_{0.25}O$(TM=Ti, V, Cr and Mn)

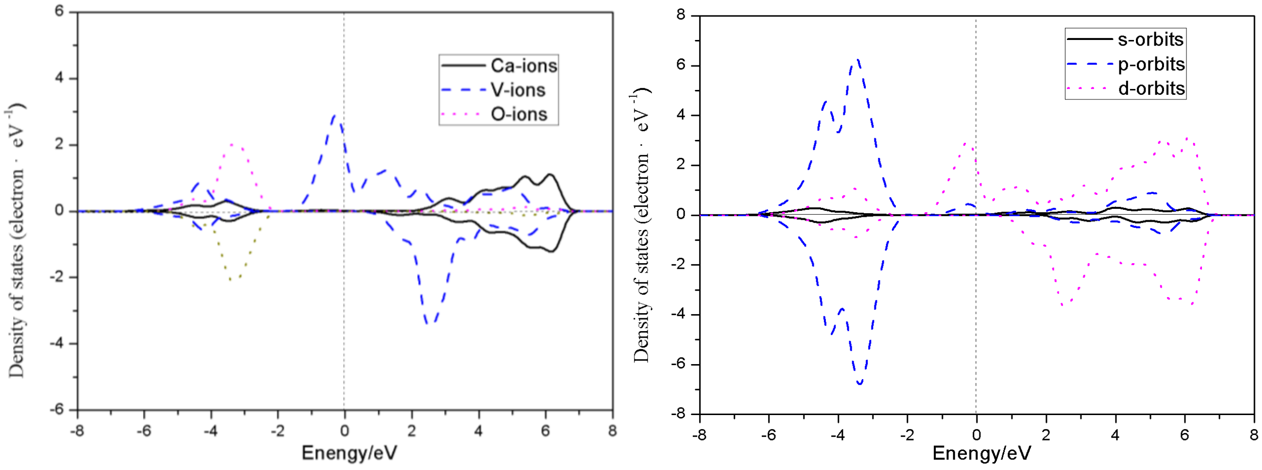
3.2 Partial and local state densities of $Ca_{0.75}V_{0.25}O$, $Ca_{0.75}Cr_{0.25}O$ and $Ca_{0.75}Mn_{0.25}O$

The partial densities of states (PDOS) and local densities of states (LDOS) of $Ca_{0.75}V_{0.25}O$, $Ca_{0.75}Cr_{0.25}O$ and $Ca_{0.75}Mn_{0.25}O$ are shown in Figs. 3(a) to (f), respectively. Here curves above and below the axial DOS=0 show the DOS of up-spin and down-spin sub-bands, respectively. The PDOS include the DOS of s, p and d-orbits and the LDOS include the DOS of one Ca-ion, one V-ion (Cr or

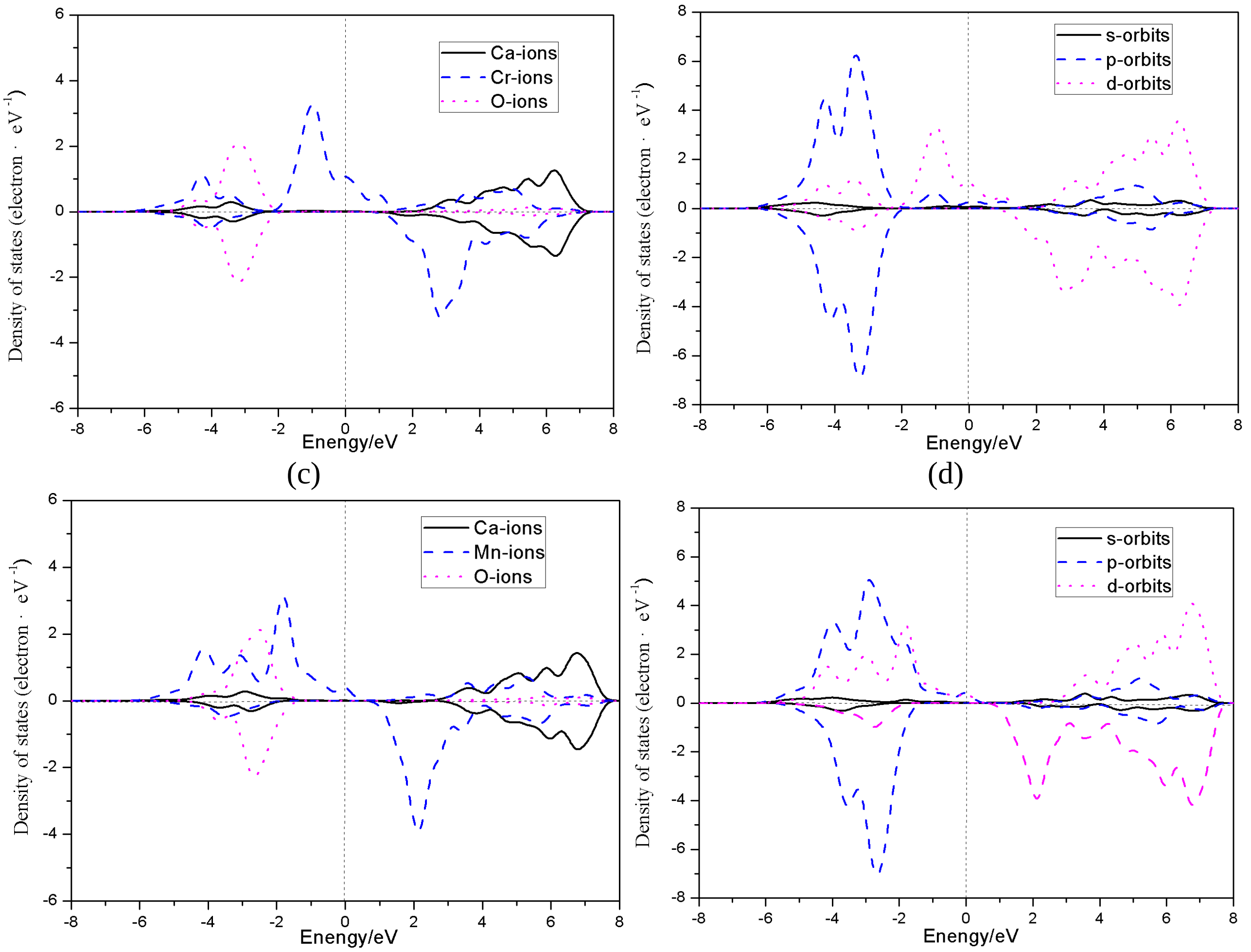
Mn) and one O-ion, respectively. In Figs. 3(a), 3(c) and 3(e), the solid lines, the dots and the dashed lines show the PDOS of s, p and d-orbits, respectively. In Figs. 3(b), 3(d) and 3(f), the solid lines, the dots and the dashed lines show the LDOS of the V- (Cr or Mn), Ca- and O-ion, respectively. Only the DOS near the Fermi level are plotted in Fig.2 and 3 because the magnetic and electric properties of HMFs are mainly influenced by the DOS near the Fermi level.

From Figs. 2 and Fig. 3 (a), the TDOS of down-spin valence bands of $Ca_{0.75}V_{0.25}O$ come mainly from p-orbits, and partially from s- and d-orbits. The PDOS of down-spin s-, p- and d-orbits are almost axially symmetrical with those of up-spin s-, p- and d-orbits when their energy is less than -1.92 eV. Therefore, they cause no influence on the magnetic and electric properties of $Ca_{0.75}V_{0.25}O$. There are only up-spin orbits through the Fermi level so that they cause the main contribution on the supercell magnetic moments and the conductivity of $Ca_{0.75}V_{0.25}O$. From Figs.2 and 3(c), there are similar TDOS and PDOS distributions for $Ca_{0.75}Cr_{0.25}O$ when the energy is less than -1.79 and through the Fermi level. However, it is evident that the energy gaps of $Ca_{0.75}Cr_{0.25}O$ are much wider than $Ca_{0.75}V_{0.25}O$. From Figs.2 and 3(e), the TDOS of down-spin valence sub-bands of $Ca_{0.75}Mn_{0.25}O$ come mainly from p- and d-orbits, and partially from s-orbits. All s-, p- and d-orbits whose energy is from -5.7 eV to -1.29 eV cause important contribution on the supercell magnetic moments. However, the contribution of s-orbits is much less than that of p- and d-orbits evidently. There are only up-spin d-orbits through the Fermi level so that they cause the main contribution on the conductivity of $Ca_{0.75}Mn_{0.25}O$, but their contribution on the supercell magnetic moments is less than orbits whose energy is from -5.6 eV to -1.29 eV.

Some ionic parameters including the number of electrons on s-, p- and d-orbits, charges and ionic magnetic moments are calculated and shown in Table 1, where ions that have same ionic parameters are put into the same line. For an example, $O_{2, 3\ 4}$ and $Ca_{1, 2, 3}$ are given for these three HMFs. From Table 1, the supercell magnetic moments of $Ca_{0.75}TM_{0.25}O$ (TM= V, Cr and Mn) are 3.00, 4.00 and 5.00 u_B after all ionic magnetic moments are added up, respectively, which arise from V- Cr- and Mn-ions.



(a) (b)



(e) (f)

Fig. 3 Spin-polarized partial and local state densities of $Ca_{0.75}TM_{0.25}O$(TM= V, Cr and Mn)

Table 1 Some calculated parameters of Ca0.75TM0.25O (TM=V, Cr and Mn)

Materials	Ions	n_s	n_p	n_d	n_t	Charge(e)	M(u_B)
$Ca_{0.75}V_{0.25}O$	O_1	1.88	5.15	0.00	7.03	-1.03	0.00
	$O_{2,3,4}$	1.88	5.04	0.00	6.92	-0.92	-0.02
	$Ca_{1,2,3}$	2.22	6.00	0.70	8.91	1.09	0.00
	V_1	2.33	6.60	3.55	12.48	0.52	3.06
$Ca_{0.75}Cr_{0.25}O$	O_1	1.88	5.15	0.00	7.03	-1.03	0.00
	O_2	1.88	5.02	0.00	6.90	-0.90	-0.06
	Ca_1	2.20	6.00	0.68	8.88	1.12	-0.02
	Cr_1	2.38	6.64	4.59	13.62	0.38	4.24
$Ca_{0.75}Mn_{0.25}O$	O_1	1.88	5.15	0.00	7.04	-1.04	0.00
	O_2	1.89	5.06	0.00	6.95	-0.95	0.08
	Ca_1	2.22	6.00	0.69	8.91	1.09	-0.02
	Mn_1	0.41	0.66	5.32	6.39	0.61	4.82

4. Conclusion

In summary, we have explored the structural, electronic and magnetic properties of $Ca_{0.75}TM_{0.25}O$ (TM= V, Cr and Mn) by performing first-principles calculations within the GGA-PBE for the exchange-correlations functional. $Ca_{0.75}TM_{0.25}O$ (TM= V, Cr and Mn) are found to be half-metallic ferromagnets. The superell magnetic moments of $Ca_{0.75}TM_{0.25}O$ (TM= V, Cr and Mn) are 3.00, 4.00 and 5.00 u_B, respectively, which arise from V-ions, Cr-ions and Mn-ions.

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