Theoretical Investigation of Structural, Electronic Properties and Half-Metallic Ferromagnetism in Ca$_{1-x}$Ti$_x$S ternary alloys

Meryem Ziati$^1$ · Hamid Ez-Zahraouy$^1$

Received: 25 January 2021 / Accepted: 11 February 2021 / Published online: 16 March 2021
© The Author(s), under exclusive licence to Springer Science+Business Media, LLC, part of Springer Nature 2021

Abstract

In this research paper, we investigated the structural, electronic, and magnetic features of titanium atom substituting calcium atom in rock-salt structure of CaS to explore the new dilute magnetic semiconductor compounds Ca$_{1-x}$Ti$_x$S. The calculations are carried out using the full potential-linearized augmented plane wave (FP-LAPW) method based on spin-polarized density functional theory (SP-DFT), implemented in WIEN2k code. The exchange and correlation potential are described by the generalized gradient approximation (PBE-GGA) and Tran-Balaha modified Becke-Johnson exchange potential (TB−mBJ). The stability of Ca$_{1-x}$Ti$_x$S ternary alloys in ferromagnetic state is provided by the total energy released from the optimized structures and defect formation energies. The classical model of Heisenberg is employed to estimate Curie temperature of these compounds. It is found that the room temperature ferromagnetism is achieved at low concentrations. The studied materials exhibit half-metallic ferromagnetic demeanor. The half-metallic gaps (GHM) are the extremely significant factors to consider for spintronic applications. The insertion of impurity significantly decreased the value of GHM due the broadening of Ti−3d states in the gap of the minority spin. Furthermore, to evaluate the effects of the exchange splitting process, the p−d exchange splitting $\Delta E_C$, $\Delta E_v$ and the exchange constants $N_{0\alpha}$, $N_{0\beta}$ are predicted.

Keywords DFT · Dilute magnetic semiconductor (DMS) · Formation energies · Half metal · Mean field approximation (MFA) · Ferromagnetic properties, Exchange splitting

1 Introduction

Semiconductors are materials which have a conductivity between conductors (metals) and non-conductors or insulators. This type of materials can be pure elements, such as silicon (Si) or germanium (Ge), or compounds such as gallium arsenide (GaAs) [1] or cadmium selenide (CdSe) [2]. To engineer their band structures and expand their usefulness, small amounts of impurities are added to pure semiconductors causing a large change in their electronic performance. This process is called “doping” or “substituting.” In general terms, transition metal (TM) doping such us (V, Cr, Mn, Fe, Co, and Ni) [3] usually generates the new bands inside the semiconductor band gap and induces magnetic properties. This category of high spin-polarized materials is called diluted magnetic semiconductors (DMSs) [4].

DMS materials have garnered enormous interest in theoretical and experimental studies due to their attractive physical properties such us magneto-electronics and magneto-transport [5]. They are mostly referred to as spin transport electron technology due to the high Curie temperatures (Tc) [6] and usually exhibit the half-metallic ferromagnetic (HMF) demeanor [7]. Half metals act as a conductor to electrons of one spin orientation, but as a semiconductor or insulator to those of the opposite orientation with 100% spin-polarized at Fermi level [8, 9]. Hence, DMS could be regarded as a potential candidate material for various technological applications, including the manufacture of photovoltaic devices, information storage, and processing devices (spintronics) [10]. To explore extensively the magnetic characteristics and using these properties in spintronic applications, the diluted magnetic semiconductors that relied on III−V, II−VI, II−IV, and IV−VI alloys, which cations are carefully substituted by transition metals, were thoroughly the subjects of numerous theoretical and experimental investigations [11–14].
CaS is part of the group II–VI alkaline earth sulfide elements that crystallize in rock salt structure, zinc blende, wurtzite, and NiAs phases [15]. In general terms, the study of the electronic properties of materials makes it possible to investigate the electronic behavior of crystalline systems and to explain the nature of the chemical bonds between atoms. The electronic properties of CaS binary compound are broadly available in the literature, where calculations are performed by many researchers using the density functional theory (DFT) through various approximations. W.Y. Ching et al. [16] and Z. Charifi et al. [17] suggested from the first-principal calculations that the electronic band gap of CaS is about 3.2 eV and 2.39 eV, respectively. Y. Kaneko et al. [1, 18] defined an indirect band gap located between Γ and X high-symmetry points for this binary compound around 4.434 eV, which is consistent with the theoretical investigations reported by M.S. Jin et al. [19] and J.G. Zhang et al. [20]. Moreover, Z.J. Chen et al. [21] proved from the band structure of CaS that the top of the valence band and the bottom of the conduction band are located at Γ point, suggesting a direct electronic band gap about 4.47 eV. However, Kravtsova et al. [22] and Saum et al. [23] stated that the electronic band gap width of CaS binary compound is around 3.5 eV and 5.38 eV, respectively, without describing its nature. On the other hand, the half-metallic ferromagnetic properties of II–VI semiconductors based DMS compounds were extensively studied using the first-principle calculations, such as V- and Cr-doped CaS reported by Hamidane et al. [24, 25], confirming the half-metallic ferromagnetism behavior in these compounds.

In the present research, we employed the first-principle theoretical methods, based on spin-polarized density functional theory (SP-DFT), to study the thermodynamic stability and to investigate the structural parameters, the electronic properties, and the half-metallic ferromagnetic features of Ca1−xTi,S ternary alloys.

2 Computational method

In this report, we have elaborated the characteristics of studied material by using the spin-polarized density functional theory (SP-DFT), which is operationalized by the full-potential linearized augmented plane wave (FP-LAPW) method [26] as implemented in Wien2K [27] ab initio simulation code. The Perdew-Burk-Ernzerhof (PBE) parameterization of the generalized gradient approximation (GGA) approach is applied to describe the exchange-correlation (XC) potential and to estimate structural, electronic, and ferromagnetic properties of Ca1−xTi,S at various concentrations (x = 0.0625, 0.125, 0.25, 0.50, and 0.75). We also apply the Tran Balaha modified Becke-Johnson (TB − mBJ) exchange approach [28] to exceed the problem posed by PBE-GGA [29] approximation which underestimates the value of the electronic band gap and also obtain optimal results.

The optimized CaS is stabilized in a rock-salt structure with space group Fm-3m (no. 225), where the Ca and S atoms occupy respectively (0, 0, 0) and (0.5, 0.5, 0.5) positions. The supercell concept is employed to achieve Ca1−xTi,S diluted magnetic semiconductor, whose objective is to study the impact of transition metal (TM) atom substitution on Ca sites.

The product of the maximum modulus of reciprocal vector \( K_{\text{max}} \) and the smallest of all atomic sphere radii \( R_{\text{MT}} \) is expanded up to a constant value (\( R_{\text{MT}} \times K_{\text{max}} = 8 \)). Inside the muffin-tin spheres, the maximum partial wave is taken at \( l_{\text{max}} = 10 \) whereas the extension of charge density is chosen at \( G_{\text{MAX}} = 14 \) (a.u.\(^{-1} \)). The muffin-tin radii (RMT) values for both Ca and Ti were 2.5 (a. u.), whereas for S is regarded as 2.2 (a. u.). In addition, an energy cutoff of \( \approx 8.0 \) Ry is implemented to get the total energy eigenvalue convergence and avoid overlapping between the valence and core states. To ensure the correct results, a Monkhorst-Pack mesh [30, 31] of \( 10 \times 10 \times 10 \) k-points are implemented in the irreducible Brillouin zone for ferromagnetic and anti-ferromagnetic calculations. Self-consistency is supposed to be reached when the total energy difference of the system converged with an accuracy of \( 10^{-6} \) Ry, and the electron charge density was set at \( 10^{-4} \) e.

3 Results and discussion

3.1 Structural properties

The calcium sulfide (CaS) is one of II–VI alkaline earth sulfide group and crystallizes in a rock-salt NaCl (B1) phase at ambient temperature [32, 33] with space group of Fm3m (no. 225) as mentioned above. In this structure, the atoms Ca and S are in the Wyckoff positions at 4a (0, 0, 0) and 4b (1/2, 1/2, 1/2), respectively. To evaluate the structural, electronic, and magnetic properties, we precisely performed the optimization of the total energy as a function of unit cell volume of CaS and Ca1−xTi,S compounds by the fitting of empirical Murnaghan’s equation of state [32]. Table 1 summarizes the expected structural parameters such as the equilibrium lattice constant (\( a_0 \)), the bulk modulus (\( B \)), and its pressure derivative (\( B' \)), according to PBE-GGA approximation. We emphasize that for the pristine CaS, the results of our calculations are slightly lower than the available experimental data and agreed reasonably with other theoretical investigations as tabulated in Table 1. However, there are no realized experimental studies.
and theoretical works to be compared with structural parameters of Ca$_{1-x}$Ti$_x$S alloys in the present work. It can further be noted from the table that substituting calcium by titanium atoms affects outstandingly the lattice constants ($a_0$) and produces a small distortion in the primitive unit cell. In fact, the observed reduction of lattice constants with increasing the concentrations $x$ of the transition metal titanium (Ti) may be ascribed to the considerable difference between Ca and Ti ionic radius. As illustrated in Fig. 1, the calculated total energies for Ca$_{1-x}$Ti$_x$S compounds in both ferromagnetic (FM) and anti-ferromagnetic (AFM) states are plotted against the volume. A comparative analysis provides lower total energy of the ferromagnetic state than the total energy found in the anti-ferromagnetic state, indicating that the FM phase is more stable than the AFM phase. Furthermore, the FM nature for all compounds is verified by the positive values of energy differences between parallel and anti-parallel spin-polarized states ($\Delta E = E_{\text{AFM}} - E_{\text{FM}}$), deduced from the self-consistent field (SCF) calculations (see Table 2). We conclude that even when the titanium concentration is gradually increased, the systems kept their ferromagnetic properties.

Moreover, Curie temperature ($T_c$) can be computed using the classical model of Heisenberg in the framework of mean field approximation (MFA) [34], according to the subsequent relation:

$$T_c = \frac{2}{3K_B} \frac{\Delta E}{x}$$

where $\Delta E$ is the energy difference between FM and AFM states, $K_B$ is the Boltzmann constant, and $x$ presents the doping concentration in the system. The predicted values of Curie temperature for the case of PBE-GGA approximation, and through the modified Becke-Johnson exchange potential are featured in Fig. 2. It can be noted from this figure that the temperature increased progressively with the doping concentration of titanium (Ti), to reach the room temperature ferromagnetism at 12.5% within the TB–mBJ approach.

### 3.2 Defect Formation Energy

Density functional theory calculations can provide valuable estimates of the thermodynamic stability with appreciable accuracy. To investigate the stability of Ti-doped CaS compound, the formation energies are computed according to the following expression [35]:

$$E_{\text{form}} = E_T(Ca_{1-x}Ti_xS) - E_T(CaS) + n_{Ca}\mu_{Ca} - n_{Ti}\mu_{Ti}$$

(2)

where $E_T(Ca_{1-x}Ti_xS)$ represents the energy of doped system, $E_T(CaS)$ denotes the total energy of pure CaS supercell, $n_{Ti}$ and $n_{Ca}$ are the numbers of introduced and removed atom, respectively, while $\mu_{Ca}$ and $\mu_{Ti}$ exhibit the chemical potentials per atom of calcium and titanium bulk crystals. As depicted in Fig. 3, defect formation energy predicted from DFT calculations at PBE-GGA functional approximation decreased with respect to increasing concentrations of titanium, whereas it seems to be more negative when the modified Becke-Johnson approach is implemented. However, the negative value of formation energy suggests that our compounds are thermodynamically stable in the ferromagnetic phase and can be readily prepared in the experiment.

### 3.3 Band Structure

The study of the electronic band structure and the density of state are essential for the semiconducting materials to identify its useful applications in various fields, by calculation of the energy band gap.

#### a- In the case of the pure material

| Compounds | $a_0$ (Å) | $B$ (GPa) | $B'$ |
|-----------|----------|----------|------|
| CaS       | 5.7132   | 5.71     | 5.68 | 55.8933 | 64 | 49 | 57.5 | 3.8860 | 4.2 | 49 | 3.8 |
| Ca$_{0.9375}$Ti$_{0.0625}$S | 5.7029 | 66.1334 | 1.7717 |
| Ca$_{0.875}$Ti$_{0.125}$S | 5.6391 | 59.2631 | 4.1843 |
| Ca$_{0.75}$Ti$_{0.25}$S | 5.5862 | 57.3976 | 1.9668 |
| Ca$_{0.50}$Ti$_{0.50}$S | 5.3667 | 62.8531 | 4.0737 |
| Ca$_{0.25}$Ti$_{0.75}$S | 5.1655 | 81.2757 | 5.0000 |

The values in the table are approximate and rounded to three significant figures.
Fig. 1 Calculated total energy optimization as a function of volume per cell of the pristine CaS and the ternary systems Ca$_{1-x}$Ti$_x$S ($x = 0.0625, 0.125, 0.25, 0.50$, and $0.75$) in both ferromagnetic and anti-ferromagnetic states.
By using PBE-GGA approximation, our calculations revealed that the pristine CaS is a semiconductor with a broad indirect band gap of 3.1522 eV, located between $\Gamma$ and $X$ high-symmetry points, as displayed in Fig. 6 and Table 3. To overcome the problem posed by PBE-GGA approximation which tends to underestimate the value of the electronic band gap [36, 37], the modified Becke-Johnson exchange potential approach is implemented. It is found that the electronic band gap is considerably

| Compounds         | $E_g$(eV) | $G_{\Gamma - \Gamma}^{HMF}$ (eV) | $G_{\Gamma - \Gamma}^{HM}$ (eV) | $\Delta E = E_{AFM} - E_{FM}$ (eV) | Behavior* |
|-------------------|-----------|----------------------------------|---------------------------------|-----------------------------------|-----------|
| PBE-GGA           |           |                                  |                                 |                                   |           |
| Ca$_{0.9375}$Ti$_{0.0625}$S | -         | 2.2998                           | 0.5336                          | 0.001690                          | HMF       |
| Ca$_{0.875}$Ti$_{0.125}$S | -         | 2.2400                           | 0.3962                          | 0.005796                          | HMF       |
| Ca$_{0.75}$Ti$_{0.25}$S  | -         | 2.0984                           | 0.1011                          | 0.018567                          | HMF       |
| Ca$_{0.50}$Ti$_{0.50}$S  | -         | -                                | -                               | 0.044160                          | Nearly HMF|
| Ca$_{0.25}$Ti$_{0.75}$S  | -         | -                                | -                               | 0.080509                          | M         |
| GGA + TB-mBJ       |           |                                  |                                 |                                   |           |
| Ca$_{0.9375}$Ti$_{0.0625}$S | -         | 3.2144                           | 1.1876                          | 0.001420                          | HMF       |
| Ca$_{0.875}$Ti$_{0.125}$S | -         | 3.1608                           | 1.0449                          | 0.004992                          | HMF       |
| Ca$_{0.75}$Ti$_{0.25}$S  | $E^\uparrow$ = 0.4155 | -                                | -                               | 0.016612                          | MS        |
| Ca$_{0.50}$Ti$_{0.50}$S  | $E^\downarrow$ = 0.6281 | -                                | -                               | 0.041205                          | MS        |
| Ca$_{0.25}$Ti$_{0.75}$S  | -         | 2.6759                           | 0.1167                          | 0.078234                          | HMF       |
| GGA + U            |           |                                  |                                 |                                   |           |
| Ca$_{0.9375}$Ti$_{0.0625}$S | -         | 3.0251                           | 1.1446                          | 0.001625                          | HMF       |
| Ca$_{0.875}$Ti$_{0.125}$S | -         | 2.8606                           | 0.9660                          | 0.004721                          | HMF       |
| Ca$_{0.75}$Ti$_{0.25}$S  | $E^\uparrow$ = 0.4047 | -                                | -                               | 0.018510                          | MS        |
| Ca$_{0.50}$Ti$_{0.50}$S  | $E^\downarrow$ = 0.5514 | -                                | -                               | 0.049407                          | MS        |
| Ca$_{0.25}$Ti$_{0.75}$S  | -         | 2.4895                           | 0.1598                          | 0.088035                          | HMF       |

*The last column shows the type of materials: MS magnetic semiconductor, HMF half-metallic ferromagnetic, M metal in both spins

By using PBE-GGA approximation, our calculations revealed that the pristine CaS is a semiconductor with a broad indirect band gap of 3.1522 eV, located between $\Gamma$ and $X$ high-symmetry points, as displayed in Fig. 6 and Table 3. To overcome the problem posed by PBE-GGA approximation which tends to underestimate the value of the electronic band gap [36, 37], the modified Becke-Johnson exchange potential approach is implemented. It is found that the electronic band gap is considerably smaller than the direct band gap calculated using other approximations. The calculated band gap, half-metallic gap, half-metallic ferromagnetic gap, and energy difference between ferromagnetic and anti-ferromagnetic states for Ca$_{1-x}$Ti$_x$S compounds are shown in Table 2.

![Fig. 2: Calculated Curie temperature ($T_c$) versus titanium concentration](image)

![Fig. 3: Calculated formation energies as a function of titanium concentration](image)
enhanced and reached the value around 4.04545 eV. It is obvious from Fig. 6 that the majority spin and the minority spin states are well overlapped suggesting the nonmagnetic performance of the pristine CaS. It is worth mentioning that the electronic behavior of the pure compound is consistent with the theoretical calculations, and experimental measurement is already reported (see Table 3) (Figs. 4 and 5).

b- In the case of the doped material

The incorporation of titanium element (TM atom) in CaS localized compound improves the probability of producing new localized electronic states in the forbidden region, leads its nature to metallic, and generates the p–d hybridization between p and d orbitals of sulfur and titanium atoms respectively, resulting a ferromagnetic behavior in the system [38, 39]. The spin-polarized band structures of ferromagnetic Ca$_{1-x}$Ti$_x$S alloys ($x = 0.0625, 0.125, 0.25, 0.50$, and 0.75) are calculated at their equilibrium lattice constants by means of PBE-GGA and TB–mBJ approximations. Along the high-symmetry directions in the first Brillouin zones, the spin-polarized band structures for Ca$_{0.9375}$Ti$_{0.0625}$S, Ca$_{0.875}$Ti$_{0.125}$S, and Ca$_{0.75}$Ti$_{0.25}$S through the generalized gradient approximation are displayed in Fig. 6. In fact, the minority spin (spin down channel) exhibits semiconducting demeanor, while the majority spin (spin up channel) presents a metallic behavior because the electronic states cross Fermi level (Ef). Therefore, the total contributions of both minority spin and majority spin states suggest the half-metallic ferromagnetic (HMF) character with 100% spin-polarized for these compounds (see Fig. 4). Hence, the half-metallic gaps (GHM) and the half-metallic ferromagnetic gaps (GHMF) are created.

Overall, the spin polarizations of the studied compounds are predicted in ferromagnetic state according to the following expression:

$$P(\%) = \frac{N_\uparrow(E_f) - N_\downarrow(E_f)}{N_\uparrow(E_f) + N_\downarrow(E_f)}$$

where $N_\uparrow(E_f)$ and $N_\downarrow(E_f)$ present the density of states for the spin up and the spin down channels, respectively, at Fermi level. The half-metallic gap (GHM) is defined as the minimum of the lowest energy conduction band and the absolute value of the highest energy valence band with respect to Fermi level of both spin states. While the half-metallic ferromagnetic gap (GHMF) corresponds to the energy difference between the upper fraction of the valence band and the minimum of the conduction band states around Fermi level at 0 eV [24, 40, 41] as clarified in Fig. 6. In the present case, the projected values of minority band gaps (GHM) and (GHMF) of the ternary alloys using PBE-GGA approximation are tabulated in Table 2. It obviously appears from these results that for the spin down configuration, the expected values of the half-metallic gaps (GHM) decrease gradually with increasing concentration $x$ of titanium due to the widening of 3d (Ti) states around the forbidden region (Ef), whereas the top of the valence band and the bottom of conduction band are situated at Γ high symmetry point providing a direct half-metallic ferromagnetic gap (GHMF). In contrast, the behavior of the Ca$_{0.50}$Ti$_{0.50}$S and Ca$_{0.25}$Ti$_{0.75}$S alloys is different from the others, which have a metallic nature in both spin states, as depicted in Fig. 6. The electronic behavior of materials is usually changed around Fermi level when the TB–mBJ approach is implemented, as illustrated in Fig. 6. Furthermore, for Ca$_{0.75}$Ti$_{0.25}$S and Ca$_{0.50}$Ti$_{0.50}$S ternary alloys, it is apparent that both the majority and minority spin states exhibit a semiconducting behavior, with an indirect band gap of about $E_{g}^{R-X} = 0.4155$ eV and $E_{g}^{X-R} = 0.6281$ eV, respectively, in the spin up channel, and a direct band gap around of $E_{g}^{R-R} = 2.8254$ eV and $2.8206$ eV, respectively, in the spin down channel along Γ–Γ direction (see Table 2).

The spin-dependent half metallicity, corresponding to a conductor in the spin up states and a semiconductor in the spin down states, is confirmed for Ca$_{0.9375}$Ti$_{0.0625}$S,

### Table 3 Calculated band gap $E_g$(eV) for CaS compound using GGA-PBE and GGA + TB-mBJ

| Present work | Other theoretical works | Experimental |
|--------------|-------------------------|--------------|
| GGA-PBE | GGA + TB-mBJ | LDA | GGA-PBE | WC-GGA | |
| $E_g^{X-R} = 3.1522$ | $E_g^{X-R} = 4.04545$ | $E_g^{X-R} = 1.9$ | $E_g^{X-R} = 2.1$ | $E_g^{X-R} = 2.1$ | $E_g^{X-R} = 5.8$ |
| $E_g^{R-X} = 3.90$ | $E_g^{R-X} = 4.25$ | $E_g^{R-X} = 4.2$ | $E_g^{R-X} = 5.34$ |

* Springer
Ca$_{0.875}$Ti$_{0.125}$S, and Ca$_{0.25}$Ti$_{0.75}$S compounds, with 100% spin-polarized behavior (presented in Fig. 5).

The half-metallic gaps (GHM) for these ternary alloys shown in Table 2 correspond to the spin down configuration. In general terms, the broad values of GHM are a good sign of half-metallic ferromagnets, as stated in reference [5]. Hence, the Ca$_{0.9375}$Ti$_{0.0625}$S and Ca$_{0.875}$Ti$_{0.125}$S with greater half-metallic gaps of about 1.1876 eV and 1.04494 eV, respectively (Table 2), are expected to be a stronger potential candidate for investigating the half-metallic ferromagnetic properties, and they can be useful for spintronic device applications.

For further clarification, the main difference encountered in the band structures between PBE-GGA and the predictable approach technique named the modified Becke-Johnson exchange potential (TB$^-$mBJ) is the enhancement of the electronic band gaps values when the last approximation is implemented. In fact, Tran et al. have demonstrated that this form of approach develops over GGA and LDA potentials for the determination of band gap values of the solids and the insulators [42]. Since bare DFT lacks accuracy on strongly correlated systems, a Hubbard corrected DFT energy function is also used to treat such a strongly correlated system effectively. The Hubbard potential with different values of $U$ is accurately optimized. At $U = 6.5$ eV, the findings suggest that there is no much discrepancy between GGA$+TB$−mBJ and GGA$+U$ band structures (see Table 2). For each concentration of titanium, Ca$_{1−x}$Ti$_x$S alloys kept the same behavior, which led to considering mBJ correction through the manuscript. Presumably, these approaches provide much improved results over the bare DFT for ground-state properties such as energy band gaps, and provide a reasonable description of electronic properties. Our results may provide beneficial guidance for further theoretical research.

### 3.4 Density of State

To further analyze the substituting effect on the electronic band structures, and to explain the origin of ferromagnetism, we calculated the total density of states (TDOS) and the partial density of states (PDOS) near the Fermi levels within PBE-GGA and the TB$−$mBJ approach, as illustrated in Figs. 4 and 5. One can perceive that the plots confirm the achieved results in the previous section. For Ca$_{0.9375}$Ti$_{0.0625}$S, Ca$_{0.875}$Ti$_{0.125}$S, and Ca$_{0.75}$Ti$_{0.25}$S at PBE-GGA potential, the minority spin states exhibit a semiconducting behavior with a broad electronic band gap, while a peak appears at Fermi level originating usually from Ti−3d states hybridized slightly with S−p states, presenting a metallic behavior, which leads to the

![Fig. 4 Spin-polarized total and partial density of states of CaS and Ca$_{1−x}$Ti$_x$S ternary alloys, using PBE-GGA approximation](image-url)
half-metallic demeanor (Fig. 4). As described in the section above, Ca$_{0.9375}$Ti$_{0.0625}$S, Ca$_{0.875}$Ti$_{0.125}$S, and Ca$_{0.25}$Ti$_{0.75}$S ternary alloys preserved the half-metallic ferromagnets, when the modified Becke-Johnson exchange potential ($TB_{mBJ}$) is applied. In fact, the total density of states (TDOS) and the partial density of states (PDOS) show, in that case, the existence of three regions:

The first region located in the valence band between $-1$ eV and $-4$ eV occurred in the mixed contributions of S $-p$ and Ti $-3d$ states for both up and down spin channels. The $p-d$ interaction between S $-p$ and Ti $-3d$ orbitals in the valence band could create the magnetism in the studied compounds generating the ferromagnetism through the exchange splitting [44]. The second region at Fermi level and the last region situated in the conduction band mainly arose from Ti $-3d$ orbitals (Fig. 5). The curves of the PDOS show that the Ti $-3d$ states split into threefold degenerate high-lying states: $d_{xy}$, $d_{xz}$, and $d_{yz}$ (linear states), and twofold degenerate low-lying states: $d_{x^2-y^2}$, $d_{x^2}$, and $d_{z^2}$ (non-linear states) under the influence of the crystal field of neighboring sulfur atoms (Figs. 4 and 5).

### 3.5 Magnetic Properties

The calculated total and local magnetic moments of Ca$_{1-x}$Ti$_x$S ($x = 0.0625$, 0.125, 0.25, 0.50, and 0.75) ternary alloys by means of PBE-GGA and the TB $-mBJ$ approach are tabulated in Table 4. Obviously, the magnetization in Ca$_{1-x}$Ti$_x$S compounds originates mainly from the Ti atom with outstanding contribution from the anion and interstitial sites. It is well known that the $p-d$ hybridization leads to local magnetic moments at Ca, S, and interstitial sites. The negative signs observed for the local magnetic moments of the sulfur antisites for all compounds bear out that the interaction between S $-p$ and Ti $-3d$ spins is anti-ferromagnetic, whereas the ferromagnetic interaction can be justified by the same magnetic signs of Ti and Ca atoms (the positive magnetic moments). The computed magnetic moments for these ternary systems became more substantial according to the gradual increase of titanium concentration.

Based on the mean field theory, we investigated using the band structures some important factors such as $s-d$ exchange constants $N_{0s}$ and $p-d$ exchange constants $N_{0p}$. These significant parameters describe, respectively, the exchange interaction between the conduction electron carriers and Ti $-3d$ states (conduction band), and the exchange interaction between the holes and Ti $-3d$ states (valence band). The $N_{0s}$
and $N_{0\alpha}$ exchange constants can be computed using the following expressions [43]:

$$N_{0\alpha} = \frac{\Delta E_C}{x < S >}$$

(4)

$$N_{0\beta} = \frac{\Delta E_V}{x < S >}$$

(5)

where $\Delta E_C = E(\downarrow) - E(\uparrow)$ and $\Delta E_V = E(\downarrow) - E(\uparrow)$ are the conduction band-edge and the valence band-edge spin-splittings, respectively, of Ca$_{1-x}$Ti$_x$S compounds at the $\Gamma$ symmetry point of the band structures. $< S >$ represents the half total magnetic moment of Ti atom [43] and $x$ is the concentration of titanium impurity. The calculated exchange constants for both potentials are tabulated in Table 5. One can clearly observe that the values of $N_{0\alpha}$ and $N_{0\beta}$ decrease as the concentration of the titanium atom increases, confirming the magnetic behavior of these ternary compounds, as mentioned in reference [5]. Additionally, the values of the exchange constants exhibit opposite signs. The positive signs of $N_{0\alpha}$ at all concentrations indicate the ferromagnetic exchange coupling between the conduction bands and the 3d states of titanium. While the negative values of $N_{0\beta}$ denote the antiferromagnetic exchange coupling between the valence bands and the Ti$^{-3d}$ states. The more negative $N_{0\beta}$ indicates a more effective spin down channel and this occurs in spin polarization systems [45].

4 Conclusion

In this paper, we investigated carefully by the mean of the spin-polarized density functional theory, the structural, electronic, and magnetic properties of Ca$_{1-x}$Ti$_x$S ternary alloys. The most important findings of the present work are as follows:

- The equilibrium lattice parameter decreases gradually with increasing concentration of titanium impurity due to the difference between the Ca and Ti atomic radii.
- The stability of the ferromagnetic states is more than the anti-ferromagnetic states, while the negative values of the formation energies irrespective of the substitution concentration lead to a thermodynamic stability.
The electronic properties calculated using PBE-GGA approximation confirm a half-metallic ferromagnetic (HMF) behavior for Ca$_{0.9375}$Ti$_{0.0625}$S, Ca$_{0.875}$Ti$_{0.125}$S, and Ca$_{0.75}$Ti$_{0.25}$S compounds. However, Ca$_{0.50}$Ti$_{0.50}$S and Ca$_{0.25}$Ti$_{0.75}$S alloys exhibit a metallic nature.

When TB$-mBJ$ is implemented, Ca$_{0.75}$Ti$_{0.25}$S and Ca$_{0.50}$Ti$_{0.50}$S ternary compounds maintain a semiconducting nature, while Ca$_{0.9375}$Ti$_{0.0625}$S, Ca$_{0.875}$Ti$_{0.125}$S, and Ca$_{0.25}$Ti$_{0.75}$S exhibit a half-metallic demeanor with 100% spin polarization at Fermi level.

The total magnetic moment rises with the increase of titanium concentration, which is mainly provided by Ti atoms.

Ca$_{1-x}$Ti$_x$S ternary alloys at low concentrations ($x = 0.0625$ and $0.125$) show a higher half-metallic gap (GHM). Hence, these compounds are predicted to be potential materials for spintronic device applications.

Our theoretical results need to be confirmed by the experiments and further theoretical investigations.

Acknowledgements The authors are thankful to Prof. P. Blaha and Prof. K. Schwarz at Wien Technical University for the Wien2k package and the group of WIEN2K for useful discussions.

### Table 4 Calculated results of total magnetic moment and local magnetic moment for Ca$_{1-x}$Ti$_x$S compounds

| Compounds     | Ca$_{0.9375}$Ti$_{0.0625}$S | Ca$_{0.875}$Ti$_{0.125}$S | Ca$_{0.75}$Ti$_{0.25}$S | Ca$_{0.50}$Ti$_{0.50}$S | Ca$_{0.25}$Ti$_{0.75}$S |
|---------------|-----------------------------|---------------------------|-------------------------|------------------------|------------------------|
| $M_{tot}$     | 3.78878                     | 3.98710                   | 4.03081                 | 7.99573                | 11.99845               |
| $M_{Ti}$      | 3.09126                     | 3.09942                   | 3.16841                 | 6.42924                | 9.75980                |
| $M_{Ca}$      | 0.04632                     | 0.08598                   | 0.05558                 | 0.06107                | 0.04531                |
| $M_{S}$       | -0.11984                    | -0.10089                  | -0.04194                | -0.09359               | -0.14725               |
| Interstitial  | 0.77104                     | 0.90260                   | 0.84876                 | 1.59901                | 2.34059                |

### Table 5 Calculated conduction and valence band-edge spin splitting $\Delta E_v$, $\Delta E_c$, and exchange constants $N_{0\alpha}$, $N_{0\beta}$ of Ca$_{1-x}$Ti$_x$S compounds for all concentrations

| Compounds     | $E_v(\uparrow)$ | $E_v(\downarrow)$ | $E_c(\uparrow)$ | $E_c(\downarrow)$ | $\Delta E_v$ | $\Delta E_c$ | $N_{0\alpha}$ | $N_{0\beta}$ |
|---------------|-----------------|-------------------|-----------------|-------------------|-------------|-------------|---------------|---------------|
| PBE-GGA       |                 |                   |                 |                   |             |             |               |               |
| Ca$_{0.9375}$Ti$_{0.0625}$S | 0.00            | -1.771            | 0.00            | 0.5336            | -1.771      | 0.533       | 5.525         | -18.34        |
| Ca$_{0.875}$Ti$_{0.125}$S  | 0.00            | -1.843            | 0.00            | 0.39626           | -1.843      | 0.396       | 2.051         | -9.547        |
| Ca$_{0.75}$Ti$_{0.25}$S   | 0.00            | -1.992            | 0.00            | 0.10113           | -1.992      | 0.101       | 0.256         | -5.044        |
| Ca$_{0.50}$Ti$_{0.50}$S   | 0.00            | 0.00              | 0.00            | 0.00              | 0.00        | 0.00        | -             | -             |
| Ca$_{0.25}$Ti$_{0.75}$S   | 0.00            | 0.00              | 0.00            | 0.00              | 0.00        | 0.00        | -             | -             |
| GGA + TB-mBJ    |                 |                   |                 |                   |             |             |               |               |
| Ca$_{0.9375}$Ti$_{0.0625}$S | 0.00            | -2.026            | 0.00            | 1.184             | -2.026      | 1.187       | 9.500         | -16.21        |
| Ca$_{0.875}$Ti$_{0.125}$S  | 0.00            | -2.115            | 0.00            | 1.044             | -2.115      | 1.044       | 4.179         | -8.463        |
| Ca$_{0.75}$Ti$_{0.25}$S   | -0.071          | -2.216            | 0.343           | 0.608             | -2.145      | 0.265       | 0.529         | -4.290        |
| Ca$_{0.50}$Ti$_{0.50}$S   | -0.157          | -2.361            | 0.470           | 0.442             | -2.203      | -0.027      | -0.014        | -1.101        |
| Ca$_{0.25}$Ti$_{0.75}$S   | 0.00            | -2.558            | 0.00            | 0.116             | -2.558      | 0.117       | 0.0045        | -0.426        |
References

1. Kaneko, Y., Koda, T.: New developments in IIa–VIb (alkaline-earth chalcogenide) binary semiconductors. J. Cryst. Growth. 86(1-4), 72–78 (1988)

2. Shukal, A., et al.: Ab initio study of structural, electronic and optical properties of Ca1−xSrxCb compounds. Phys. B Condens. Matter. 404(21), 3964–3972 (2009)

3. Sharma, V.K., Xalbo, R., Varma, G.D.: Structural and magnetic studies of Mn-doped ZnO. Cryst. Res. Technol. 42(1), 34–38 (2007)

4. Yogeswari, M., Kalpana, G.: Electronic structure and half-metallic ferromagnetism in (C, Si, Ge and Sn) doped alkaline-earth sulfides: a first principles approach. J. Alloys Compd. 573, 83–89 (2013)

5. Abelli, Z., et al.: Theoretical investigation of the electronic structure and magnetic properties in ferromagnetic rock-salt and zinc blende structures of 3 d (V)-doped MgS. J. Electron. Mater. 48(6), 3794–3804 (2019)

6. Doumi, B., et al.: First-principle investigation of half-metallic ferromagnetism in octahedronally bonded Cr-doped rock-salt SrS, SrSe, and SrTe. Eur. Phys. J. B. 88(4), 1–9 (2015)

7. Bernh, K., et al.: Theoretical investigation of electronic performance, half-metallicity, and magnetic properties of Cr-substituted BaTe. J. Comput. Electron. 17(3), 909–919 (2018)

8. Katsnelson, M.I., et al.: Half-metallic ferromagnets: from band structure to many-body effects. Rev. Mod. Phys. 80(2), 315 (2008)

9. De Groot, R.A., et al.: New class of materials: half-metal ferromagnets. Phys. Rev. Lett. 50(25), 2024 (1983)

10. Mahmood, Q., et al.: First-principles evaluation of Co-doped ZnS and ZnSe semi-conducting ferromagnets. J. Alloys Compd. 688, 899–907 (2016)

11. Obeid, M.M., Edrees, S.J., Shukur, M.M.: Synthesis and characterization of pure and cobalt doped magnesium oxide nanoparticles: Insight from experimental and theoretical investigation. Superlattice. Micro. 122, 124–139 (2018)

12. De Paiva, R., Nogueira, R.A., Alves, J.L.A.: Theoretical study of dilute GaN–4d transition metal alloys. J. Phys. Condens. Matter. 18(37), 8589 (2006)

13. Singh, J., Kumar, S., Verma, N.K.: Effect of Ni-doping concentration on structural, optical and magnetic properties of CdSe nanorods. Mater. Sci. Semicon. Process. 26, 1–6 (2014)

14. Saikia, D., Borah, J.P.: Ferromagnetic ordering in chemically synthesized ZnS: Mn doped magnetic semiconductor: a density functional theory explanation. Phys. Lett. A. 381(44), 3743–3746 (2017)

15. Chouti, H., et al.: Spin-polarized investigation of ferromagnetism on magnetic semiconductors MnxCa1−xS in the rock-salt phase. Mater. Chem. Phys. 148(3), 1000–1007 (2014)

16. Ching, W.Y., Gan, F., Huang, M.-Z.: Band theory of linear and nonlinear susceptibilities of some binary ionic insulators. Phys. Rev. B. 52(3), 1596 (1995)

17. Charifi, Z., et al.: High pressure study of structural and electronic properties of calcium chalcogenides. J. Phys. Condens. Matter. 17(26), 4083 (2005)

18. Dadsetani, M., Pourghazi, A.: Optical properties of strontium monochalcogenides from first principles. Phys. Rev. B. 73(19), 195102 (2006)

19. Jin, M.-S., et al.: Optical properties of undoped and Co+ 2+ doped CaS, CaSe, BaS, and BaSe single crystals. J. Korean Phys. Soc. 39(1), 692–697 (2001)

20. Zhang, J.-G., et al.: Photoluminescence and optical absorption in CaS: Eu 2+: Sm 3+ thin films. J. Mater. Res. 7(2), 411–417 (1992)

21. Chen, Z.J., Xiao, H.Y., Zu, X.T.: Structural and electronic properties of CaS Crystal: a density functional theory investigation. Phys. B Condens. Matter. 391(1), 193–198 (2007)

22. Krvatsova, A.N., et al.: Electronic structure of M S (M = Ca, Mg, Fe, Mn): X-ray absorption analysis. Phys. Rev. B. 69(13), 134109 (2004)

23. Saum, G.A., Hensley, E.B.: Fundamental optical absorption in the IIa-VIB compounds. Phys. Rev. 113(4), 1019 (1959)

24. Hamidane, O., Meddour, A., Bourouis, C.: Half-metallic ferromagnetism character in Cr-doped CaS diluted magnetic insulator and semiconductor: an ab initio study. J. Supercond. Nov. Magn. 32(7), 2155–2164 (2019)

25. Hamidane, N., et al.: Ab initio full-potential study of the structural, electronic, and magnetic properties of the cubic Sr 0.75 Ti 0.25 X (X = S, Se, and Te) ternary alloys. J. Supercond. Nov. Magn. 33(10), 3263–3272 (2020)

26. Hohenberg, P., Kohn, W.J.P.R.: Density functional theory (DFT). Phys. Rev. 136, B864 (1964)

27. Blaha, P., et al.: wien2k. An augmented plane wave+ local orbitals program for calculating crystal properties. (2001)

28. Tran, F., Blaha, P.: Accurate band gaps of semiconductors and insulators with a semilocal exchange-correlation potential. Phys. Rev. Lett. 102(22), 226401 (2009)

29. Perdew, J.P., Burke, K., Ernzerhof, M.: Generalized gradient approximation made simple. Phys. Rev. Lett. 77(18), 3865 (1996)

30. Monkhorst, H.J., Pack, J.D.: Special points for Brillouin-zone integrations. Phys. Rev. B. 13(12), 5188 (1976)

31. Addadi, Z., et al.: Electronic and ferromagnetic properties of 3d (V)-doped (BaS) barium sulfide. J. Supercond. Nov. Magn. 30(4), 917–923 (2017)

32. Luo, H., et al.: Structural phase transformations and the equations of state of calcium chalcogenides at high pressure. Phys. Rev. B. 50(22), 16232 (1994)

33. Jha, P., Sakalle, U.K., Sanyal, S.P.: Pressure induced structural phase transition in MgS and CaS. J. Phys. Chem. Solids. 59(5), 599–603 (1998)

34. Sato, K., Dedeliers, P.H., Katayama-Yoshida, H.: Curie temperatures of III–V diluted magnetic semiconductors calculated from first principles. EPL (Europhysics Letters). 61(3), 403 (2003)

35. Khan, M.S., et al.: Effect of Vanadium doping on optoelectronic and magnetic properties of wurzite ZnS crystal. Optik. 204, 164162 (2020)

36. Djelal, A., et al.: Ab-initio DFT–FP-LAPW/TP–mBJ/LDA–GGA investigation of structural and electronic properties of Mg5xZn1−xO alloys in Wurtzite, Rocksalt and Zinc-Blende phases. Superlattice. Micro. 109, 81–98 (2017)

37. Heyd, J., et al.: Energy band gaps and lattice parameters evaluated with the Heyd-Scuseria-Ernzerhof screened hybrid functional. J. Chem. Phys. 123(17), 174101 (2005)

38. Sato, K., et al.: First-principles theory of dilute magnetic semiconductors. Rev. Mod. Phys. 82(2), 1633 (2010)

39. Sarkar, A., et al.: Defect driven ferromagnetism in Sn02: a combined study using density functional theory and positron annihilation spectroscopy. RSC Adv. 5(2), 1148–1152 (2015)

40. Yao, K.L., et al.: Half-metallic ferromagnetism of zinc-blende CrS and CrP: a first-principles pseudopotential study. Solid State Commun. 133(5), 301–304 (2005)

41. Gao, G.Y., et al.: Half-metallic ferromagnetism in zinc-blende CaC, ScC, and BaC from first principles. Phys. Rev. B. 75(17), 174442 (2007)
42. Tran, F., Blaha, P., Schwarz, K.: Band gap calculations with Becke–Johnson exchange potential. J. Phys. Condens. Matter. 19(19), 196208 (2007)

43. Bahloul, H., et al.: Electronic structures and ferromagnetic properties of 3d (Cr)-doped base barium selenide. J. Supercond. Nov. Magn. 32(7), 2185–2192 (2019)

44. Mahmood, Q., et al.: The study of electronic, elastic, magnetic and optical response of Zn1-\textit{x}Ti\textit{Y} (Y = S, Se) through mBJ potential. Curr. Appl. Phys. 16(5), 549–561 (2016)

45. Mahmood, Q., Hassan, M.: Systematic first principle study of physical properties of Cd0.75Tix0.25Z (Z = S, Se, Te) magnetic semiconductors using mBJ functional. J. Alloys Compd. 704, 659–675 (2017)

Publisher’s note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.