Promising electronic structure of double perovskite Sr₂TiMoO₆: Spin-polarized DFT+U approach

Yang Jian HUI, Fan Qiang*
School of Physics and Electronic Engineering, Leshan Normal University, Leshan, Sichuan 614004, China
Email: fq1893@foxmail.com

Abstract: The electronic structure of double perovskite Sr₂TiMoO₆ have been systematically investigated using first principle. The spin-polarized electronic band structure and the density of states reveal that the spin-up channel has metal behavior while the spin-down channel expresses semiconductor behavior with direct band gap of 2.92 eV. For valence band, the O-2p states is the mainly contributor for both spin-up and spin-down channels above -5.3 eV. Between -7.7 eV to -5.3 eV, valence band is formed by O-2p states with admixture of Mo-4d states. For conduction band, from range 4 eV to 7.4 eV is mostly formed by Sr-3d. On the other hand, O-2p, Mo-4d as well as Ti-3d states mainly consists of the conduction band near Fermi energy, so those states need to be more concerned. The spin splitting may lead to unusual thermoelectric transport properties.

1. Introduction
Double perovskites A₂BB’O₆ (where A respects alkali earth metal or rare-earth element, B and B’ are transition elements with electronic configuration in d-orbital) has double unit cell of normal perovskite. Numerous structure types and extensively useful properties have been widely investigated by using different elements on A, B or B’ sites. Double perovskites materials are exploited in a variety of physical properties such as half metallic [1], optoelectronic [2, 3] magnetocaloric [4, 5], antiferromagnetic [6], ferromagnetic [7], making their widely used in spintronic and optoelectronic devices [8, 9]. In addition, double perovskites have been attracted attentions for thermoelectric performance due to good durability and low synthesis cost [10-13]. Because of high electronic conductivity and low thermal conductivity, double perovskite Sr₂TiMoO₆ exhibits as promising thermoelectric material [14, 15]. The absence of the electronic structure of double perovskite Sr₂TiMoO₆ makes it is necessary to predict theoretically. We systematically studied the electronic structure of double perovskite Sr₂TiMoO₆ based on the framework of density functional theory (DFT). The computational methods and details are presented as follows.

2. Computational Methods and details
The structure of solid state material can be obtained not only from experiment but also from theory. In theoretically, structure of double perovskite A₂BB’O₆ can be verified by the tolerance factor (Tₚ), which is defined using the following formula:

\[ T_p = \frac{R_A + R_O}{\sqrt{2}(\frac{R_B + R_B'}{2} + R_O)} \]

where \( R_A, R_B, R_B', R_O \) are the ionic radius of A, B, B’ and O atoms respectively. With increase of \( T_p \)
in the range from 0.78 to 1.05, the compound crystal structure of double perovskite comes from orthorhombic, tetragonal, and cubic to hexagonal. The double perovskite is cubic structure with Fm3m space group (225) as $T_f \approx 1$ [10, 16, 17]. The $T_f$ and the crystal structure of double perovskite Sr$_2$TiMoO$_6$ have been predicted using the Structure Prediction Diagnostic Software (SPuDS) [18, 19]. There are 40 atoms in conventional unit cell of double perovskite Sr$_2$TiMoO$_6$. The crystal structure of Sr$_2$TiMoO$_6$ is shown in Figure 1. The Wyckoff positions of Sr, Ti, Mo, O are located at 8c(1/4, 1/4, 1/4), 4a(0, 0, 0), 4b(1/2, 0, 0), 24e(0.2456, 0, 0), respectively. The electronic structure calculations are performed using spin-polarized density functional theory (DFT) under generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) functional form [20] with plane wave pseudo potential method as implemented in Vienna Ab-initio Simulation Package (VASP) code [21, 22]. For Brillouin zone integration, Monkhorst-Pack grid of 11×11×11 k-mesh with Γ centered is used. The plane wave cutoff energy is set to 450 eV and energy convergence threshold is $10^{-6}$ eV. The maximal force on each atom is less than 0.01 eV/Å for optimizing lattice constants and atomic positions. To overcome the well-known underestimated band gap problem of d-electron, the GGA + U correction is adopted to treat the strong correlation for d-electrons of titanium and molybdenum. In GGA+U correction, the two-electron integrals of Hartree–Fock treatment are expressing in terms of U and J parameters, where U and J adjust the strength of the on-site Coulomb and exchange interaction inter, respectively. The values of $U = 8.2$ eV and $J = 1.0$ eV are used for titanium 3d electrons from previous understanding about electronic structure of titanium dioxide [23]. The values of $U = 3.0$ eV and $J = 0.89$ eV were used for molybdenum 3d electrons from previous work about molybdenum double perovskite [24].

![Figure 1 Crystal structure of double perovskite Sr$_2$TiMoO$_6$](image)

3. Results and discussions

The structural parameters are computed by minimizing the total energy for several volumes around equilibrium volume. The calculated total energy of cubic double perovskite Sr$_2$TiMoO$_6$ versus different cell velum is shown in Figure 2, together with the fitted curve using the Birch-Murnaghan equation of state [25]. The optimizing equilibrium lattice constant is 7.938Å, which is reported for the first time from first principle calculation.
Figure 2 Total energy versus cell volume for Sr₂TiMoO₆

The spin-orbital coupling band structure along the high-symmetry in the first Brillouin zone (1BZ) and total density of states (TDOS) for double perovskite Sr₂TiMoO₆ employing by GGA +U is displayed as in Figure 3.

Figure 3 Band structure and TDOS of Sr₂TiMoO₆ (dashed line denotes Fermi energy)

The spin splitting is obvious observed between spin-up and spin-down bands. It is unambiguous a few spin-up bands (overlap from -1.35eV to 0.45eV with bandwidth of 1.80eV) crossing the Fermi level. That is to say the spin-up channel observed metallic nature. The spin-down channel expresses semiconductor behavior for the reason of the Fermi level is located at forbidden band gap. Both valence band maximum (VBM) and conduction band minimum (CBM) are situated at Γ point with band gap of 2.92 eV. Therefore, the double perovskite Sr₂TiMoO₆ has half metallic (HM) nature as many double perovskite including transition elements [1, 26-29].

To aid in understanding the character of electronic structure, we calculated the partial densities of states (PDOS) and total densities of states (TDOS) for spin-up and spin-down channels of double perovskite Sr₂TiMoO₆ and displayed them together in Figure 4.
As can be seen from Figure 4, for valence band (VB), the O-2p states is the mainly contributor for both spin-up and spin-down channels above -5.3eV. Between -7.7eV to -5.3eV, VB is formed by O-2p states with admixture of Mo-4d states. We can see that conduction band (CB) from range 4 eV to 7.4 eV is mostly formed by Sr-3d. On the other hand, O-2p, Mo-4d as well as Ti-3d states mainly consists of the CB near Fermi energy, so those states need to be more concerned. As is well known, for octahedral complex, the octahedral crystal field can split d levels of central atom from five-fold degenerate to doubly degenerate \(eg(d_{x^2-y^2}, d_z^2)\) and triple degenerate \(t\_2g(d_{xy}, d_{xz}, d_{yz})\). Moreover, the \(e_g\) state lies higher in energy than \(t\_2g\) state. The MoO\(_6\) and TiO\(_6\) octahedral structures of double perovskite Sr\(_2\)TiMoO\(_6\) may result in splitting of the Mo-\(d\) and Ti-\(d\) levels to \(e_g\) and \(t\_2g\) states as denoted in Figure 4. The metallic behavior for spin-up channel comes from the hybridization of O-2p and Mo-\(t\_2g\). The main contribution from range 1.4 eV to 4.7 eV for spin-up channel is due to Ti-\(t\_2g\) states with some admixture of O-2p states. While as regards for the CB near Fermi energy of spin-down channel can be attributed to hybridization of Ti-\(t\_2g\), Mo-\(t\_2g\) and O-2p states.

4. Conclusions

Summarily, the electronic structures of double perovskite Sr\(_2\)TiMoO\(_6\) are calculated using first principle within preferential spin-polarized DFT+U approach. The thermoelectric performances of double perovskite Sr\(_2\)TiMoO\(_6\) are predicted using Boltzmann transport theory within constant relaxation time approximation based on spin-polarized electronic structure. The electronic structures illustrate the spin splitting is obvious observed between spin-up and spin-down bands. The spin-up channel has metal behavior while the spin-down channel expresses semiconductor behavior with direct band gap of 2.92 eV.

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