

Potential thermoelectric material $\text{Sr}_2\text{TiMoO}_6$ from ab initio calculations

Fan QIANG, Yang Jian HUI*

School of Physics and Electronic Engineering, Leshan Normal University, Leshan, Sichuan 614004, China

Email: yjh20021220@foxmail.com

Abstract: The thermoelectric properties of double perovskite $\text{Sr}_2\text{TiMoO}_6$ have been systematically proposed by using semi-classic Boltzmann transport theory based on the electronic structure from first principle. The transport properties for the spin-up and spin-down electrons of double perovskite $\text{Sr}_2\text{TiMoO}_6$ compounds have been demonstrated. The metallic spin-up channel results in considerable electronic conductivity. For the big band gap, there are small electronic conductivity and zero Seebeck coefficients at low temperatures for semiconducting spin-down channel. The optimal ZT values at 900 K reach to 1.28 and 1.35 for p-type doping and n-type doping, respectively. Considering the ZT value is sizable, double perovskite $\text{Sr}_2\text{TiMoO}_6$ is a potential candidate in thermoelectric device.

1. Introduction

Researchers pay close attention to thermoelectric materials due to which can convert directly the waste heat into useful electrical energy [1, 2]. The conversion efficiency between heat and electricity of thermoelectric material is defined by a dimensionless figure of merit (ZT), which is identified as: $ZT = S^2\sigma T / (k_e + k_l)$, where S , σ and T are Seebeck coefficient, electrical conductivity and temperature respectively. k_e and k_l are thermal conductivities contributed from electron and lattice respectively. $S^2\sigma$ is named power factor (PF) of thermoelectric material. Improving PF and decreasing thermal conductivity are typical ways to achieve high thermoelectric performance with large ZT value. However, it is technically difficult to optimize the ZT value for the coupling of S , σ through carrier concentration. The discovery of new materials with high thermoelectric performance has been pursued by materials designers.

The new thermoelectric material of double perovskite $\text{A}_2\text{BB}'\text{O}_6$ consisting of double unit cell of normal perovskite (ABO_3 and $\text{AB}'\text{O}_3$) is a new study field. Usually, A is alkali earth metal or rare-earth element; B and B' are transition elements with d-orbital electronic configuration. Recently, Saxena .et al [3, 4] reported double perovskite $\text{Sr}_2\text{TiMoO}_6$ has shown great potential for thermoelectric applications with metal like electronic conductivity (10^5S/m) and low thermal conductivity ($5.8\text{-}7.5\text{ Wm}^{-1}\text{K}^{-1}$). The thermal conductivity of $\text{Sr}_2\text{TiMoO}_6$ is lower than that of pure SrTiO_3 ($6\text{-}11\text{ Wm}^{-1}\text{K}^{-1}$) [5, 6]. Meanwhile, the electric conductivity of $\text{Sr}_2\text{TiMoO}_6$ is larger than that of pure SrTiO_3 ($<10^4\text{S/m}$) [6]. However, so far as I know, the thermoelectric property of double perovskite $\text{Sr}_2\text{TiMoO}_6$ has not been done from theoretical research. Motivated by the above, we address the thermoelectric property of double perovskite $\text{Sr}_2\text{TiMoO}_6$ from first principles in order to provide reference data for further experimental and theoretical research. The computational methods and details are presented as follows.



2. Computational Methods

Based on the electronic structure, the thermoelectric transport properties are calculated using Boltzmann transport theory as implemented in BoltzTraP code within constant relaxation time approximation [7]. 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 [8] with plane wave pseudo potential method as implemented in Vienna Ab-initio Simulation Package (VASP) code [9, 10]. $11 \times 11 \times 11$ k-mesh with Γ centered in Monkhorst-Pack grid is used in Brillouin zone integration. The plane wave cutoff energy is set to 450 eV and energy convergence threshold is set to 10^{-6} eV. For optimizing lattice constants and atomic positions, the maximal force on each atom is less than 0.01 eV/Å.

The GGA + U correction is adopted to overcome the well-known underestimated band gap problem of d-electron and get more reliable electronic structure. 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 [11]. 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 [12].

3. Results and discussions

The structure of double perovskite $\text{Sr}_2\text{TiMoO}_6$ is composed of three-dimensional framework of alternating MoO_6 and TiO_6 octahedrons, with Sr-cations filling interstitial spaces between MoO_6 and TiO_6 octahedrons as shown in Figure 1.

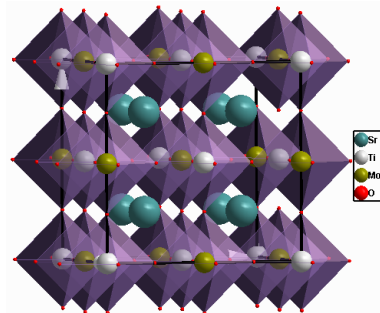


Figure 1 The crystal structure of double perovskite $\text{Sr}_2\text{TiMoO}_6$

The spin-orbital coupling band structure calculated by GGA +U for double perovskite $\text{Sr}_2\text{TiMoO}_6$ is plotted in Figure 2.

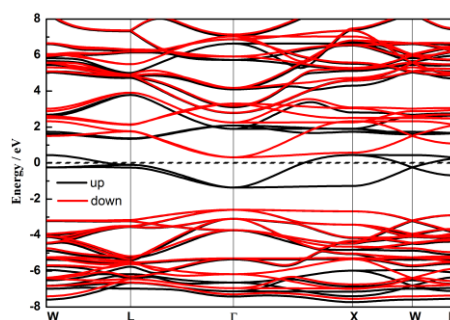


Figure 2 Band structure of $\text{Sr}_2\text{TiMoO}_6$ (black line presents spin-up channel, red line denotes spin-up channel, Fermi energy is set at zero)

The spin-down channel expresses semiconductor behavior with direct band gap of 2.92 eV, meanwhile, the spin-up channel observes metallic nature which will lead to large electrical conductivity.

By using semi-classical Boltzmann transport theory within constant relaxation time approximation,

the transport coefficients can be derived from pervious spin-polarized electronic eigenvalues. The Seebeck coefficient (S) and electronic conduction with respect to scattering time (σ/τ) can be directly calculated using Boltzmann transport theory [7] as following formulas:

$$S(T) = \frac{\int_{-\infty}^{\infty} dE \sigma(E) (E - \mu) \partial f / \partial E}{T \int_{-\infty}^{\infty} dE \sigma(E) \partial f / \partial E},$$

$$\sigma(E) = N(E) v^2(E) \tau(E)$$

where f , T , μ are the Fermi-Dirac distribution function, temperature and chemical potential, respectively. τ , N , v represent relaxation time, carrier concentration and group velocity, respectively. The total electronic conductivity and Seebeck coefficient are calculated by using current model as in recent works [13-16].

The calculated Seebeck coefficient (S) of $\text{Sr}_2\text{TiMoO}_6$ in both spin-up and spin-down channels as a function of chemical potential (μ) at different temperature is plotted in Figure 3.

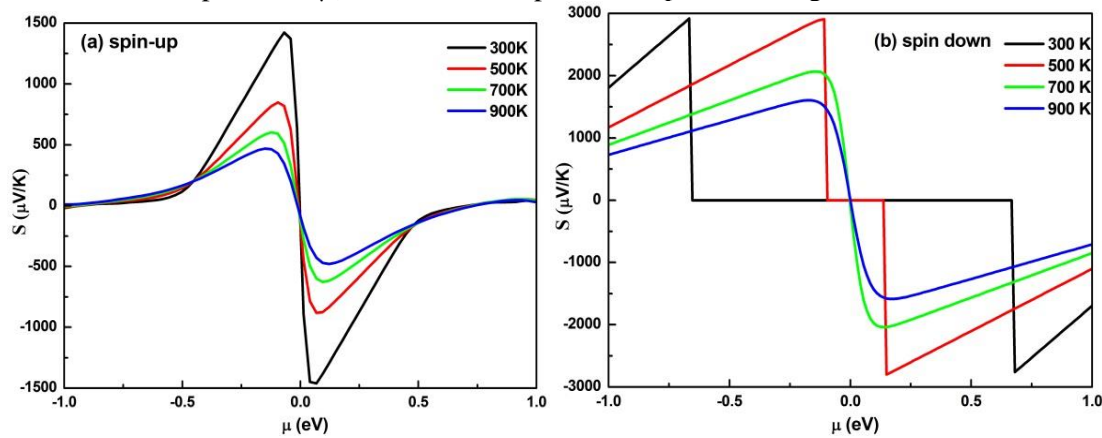


Figure 3 Seebeck coefficient (S) of $\text{Sr}_2\text{TiMoO}_6$ as a function of chemical potential (μ) at different temperature (a) spin-up channel, (b) spin-down channel

Glance at figure 3, we find that the Seebeck coefficient (S) is very sensitive to temperature and chemical potential. The sign of S indicates the type of major charge carries, S with positive represents p-type doping, whereas n-type doping have negative S . The temperature has important influence on S in the chemical potential range from -0.5 eV to 0.5 eV for spin-up channel. The curves tend rapidly to zero outside range from -0.5eV to 0.5 eV. Generally, the maximum of S is obtained at 300 K and S decreases with the increasing of temperature at a certain chemical potential in the chemical potential range from -0.5eV to 0.5 eV.

It is need emphasized the for spin-down channel, the values of S equal to zero in the chemical potential range from -0.65eV to 0.65 eV for big band gap of spin-down channel. Moreover, the range of chemical potential for $S = 0$ becomes narrower with the increasing of temperature for the major reason of electronic excitation become easy with increasing of temperature.

As well known, within constant relaxation time approximation, the electronic conduction (σ) can't be obtained directly from Boltzman transport theory. In Figure 4, the electrical conductivity over relaxation time (σ/τ) and power factor ($\text{PF} = S^2\sigma/\tau$) are presented at different temperature as a function of chemical potential.

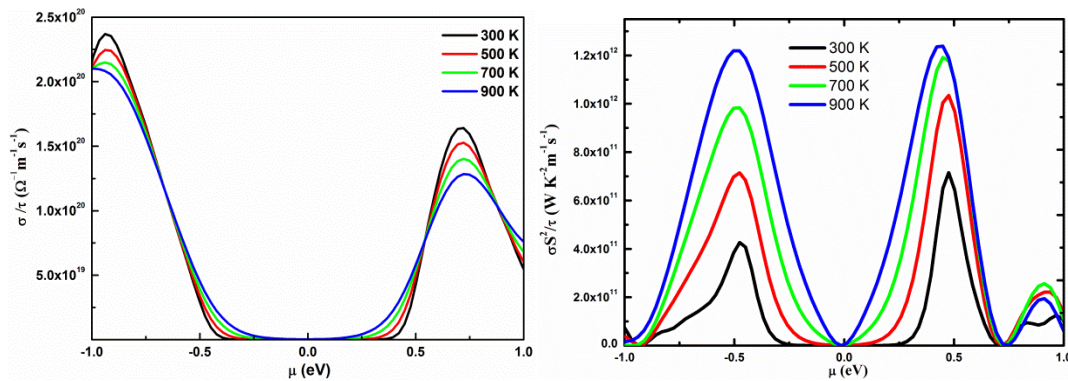


Figure 4 The electrical conductivity over relaxation time (σ/τ) and power factor ($PF = S^2\sigma/\tau$) as a function of chemical potential at different temperature

As we can see from the Figure 4, the maximum σ/τ for p-type is larger than that of n-type. Combined with Seebeck coefficient, the power factor ($S^2\sigma/\tau$) are also plotted in figure 4.

The power factor obtain maximum at about ± 0.5 eV chemical potential. The variation of power factor rate to relaxation time ($\sigma S^2/\tau$) as function of temperature at $\mu = \pm 0.5$ eV is depicted in Figure 5.

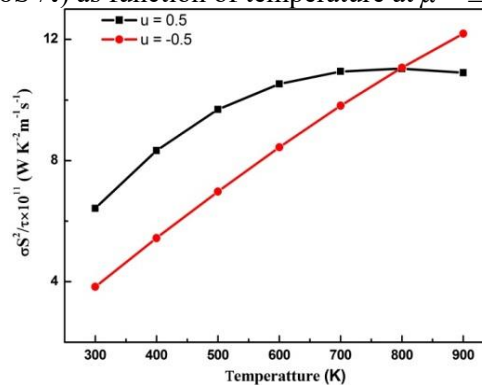


Figure 5 Calculated $\sigma S^2/\tau$ as function of temperature at $\mu = \pm 0.5$ eV

The value of power factor for $\mu = 0.5$ eV is larger than that for $\mu = -0.5$ eV below 800 K. The value of power factor for $\mu = -0.5$ eV increases linearly with increased temperature from about 3.83×10^{11} W/K²m⁻¹s⁻¹ at 300 K to 1.22×10^{12} W/K²m⁻¹s⁻¹ at 900 K.

It is difficult to accurately estimate the relaxation time (τ) for electrons due to complex scattering mechanisms must to consider at different temperature. The relaxation time for bulk materials is about 10^{-14} s to 10^{-15} s[15], it is reasonable to choose the relaxation time as a constant [17], 1×10^{-14} s are used to get the electrical conductivity. The lattice thermal conductivity (K_L) is an important factor for the thermoelectric performance of material. The K_L is employed from experimental data [4]. The electrical thermal conductivities are calculated by the Wiedemann-Franz law $k_e = \sigma LT$, where L , σ , T are Lorenz number, electrical conductivity and temperature in Kelvin, respectively. The possible ZT of double perovskite $\text{Sr}_2\text{TiMoO}_6$ with respect to chemical potential are shown in Figure 6.

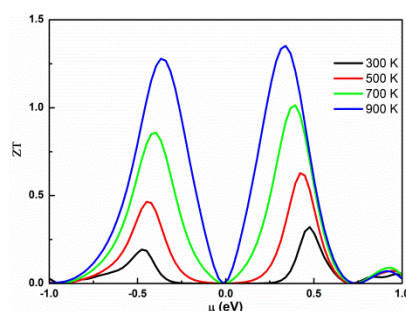


Figure 6 Calculated ZT of $\text{Sr}_2\text{TiMoO}_6$ as a function of chemical potential (μ) at different temperature

It is found that both the p-type doping and n-type doping show almost equivalent thermoelectric behaviors due to the rather similar ZT value at the same doping. The optimal ZT values for p-type doping and n-type doping at 300 K are 0.14 and 0.19, respectively. The optimal ZT values reach to 1.28 and 1.35 for p-type doping and n-type doping at 900 K.

4. Conclusions

The Seebeck coefficient (S) and electronic conductivity ratio in relaxation time for both spin-up and spin-down channels have been calculated. The spin-polarized effect has significantly influence on thermoelectric performances. The metallic spin-up channel results in considerable electronic conductivity. For the big band gap, there are small electronic conductivity and zero Seebeck coefficients at low temperatures for semiconducting spin-down channel. The total power factor rate to relaxation time is obtained from two spin channels. The optimal ZT values reach to 1.28 and 1.35 for p-type doping and n-type doping at 900 K. The results show that double perovskite $\text{Sr}_2\text{TiMoO}_6$ is good for thermoelectric material.

Acknowledgements

This work is supported from the Scientific Research Foundation of the Education Department of Sichuan Province (No. 17ZA0195), the Open Research Fund of Computational Physics Key Laboratory of Sichuan Province, Yibin University (No. JSWL2015KF01), Leshan Normal University Research Program, China (No. Z16016) and Science and Technology Bureau of Leshan city (No. 17GZD048).

References

- [1] Gorai P, Stevanović V, Toberer E S. Computationally guided discovery of thermoelectric materials[J]. *Nature Reviews Materials*, 2017, 2: 17053.
- [2] Tan G, Zhao L, Kanatzidis M G. Rationally Designing High-Performance Bulk Thermoelectric Materials[J]. *Chem. Rev.*, 2016, 116(19): 12123-12149.
- [3] Saxena M, Tanwar K, Maiti T. Environmental friendly $\text{Sr}_2\text{TiMoO}_6$ double perovskite for high temperature thermoelectric applications[J]. *Scripta Mater.*, 2017, 130: 205-209.
- [4] Saxena M, Maiti T. Effect of Ba-doping on high temperature thermoelectric properties of $\text{Sr}_2\text{TiMoO}_6$ double perovskites[J]. *J. Alloy. Compd*, 2017, 710: 472-478.
- [5] Cain T A, Kajdos A P, Stemmer S. La-doped SrTiO_3 films with large cryogenic thermoelectric power factors[J]. *Appl. Phys. Lett.*, 2013.
- [6] Muta H, Kurosaki K, Yamanaka S. Thermoelectric properties of reduced and La-doped single-crystalline SrTiO_3 [J]. *J. Alloy. Compd*, 2005, 392(1-2): 306-309.
- [7] Madsen G K H, Singh D J. BoltzTraP. A code for calculating band-structure dependent quantities[J]. *Comput. Phys. Commun.*, 2006, 175(1): 67-71.
- [8] Perdew J P, Burke K, Ernzerhof M. Generalized Gradient Approximation Made Simple[J]. *Phys. Rev. Lett.*, 1997, 78: 1396.
- [9] Kresse G, Furthmüller J. Efficient iterative schemes for ab initio total-energy calculations using a

- plane-wave basis set[J]. Phys. Rev. B Condens Matter, 1996, 54(16): 11169-11186.
- [10] Kresse G. From ultrasoft pseudopotentials to the projector augmented-wave method[J]. Phys. Rev. B, 1999, 59(3): 1758-1775.
- [11] Meng Q, Wang T, Liu E, Ma X, Ge Q, Gong J. Understanding electronic and optical properties of anatase TiO₂ photocatalysts co-doped with nitrogen and transition metals[J]. Phys. Chem. Chem. Phys., 2013, 15: 9549-9561.
- [12] M. Musa S H E. La-doping effects on structural, electronic and magnetic properties of Ba_{2-x}La_xCrMO₆ (M = Mo, Nb): LMTO-PLW+ (LSDA+U) study[J]. Mater. Chem. Phys., 2014, 145(1-2): 36-43.
- [13] Yousuf S, Gupta D C. Insight into electronic, mechanical and transport properties of quaternary CoVTiAl: Spin-polarized DFT+U approach[J]. Materials Science and Engineering: B, 2017, 221: 73-79.
- [14] Reshak A H. Thermoelectric properties of TbFe₂ and TbCo₂ in C15- laves phase: Spin-polarized DFT+U approach[J]. J. Magn. Magn. Mater., 2017, 422: 287-298.
- [15] Yang J H, Fan Q, Cheng X. Prediction for electronic, vibrational and thermoelectric properties of chalcopyrite AgX(X=In,Ga)Te₂: PBE + U approach[J]. Royal Society Open Science, 2017, 4(10): 170750.
- [16] Yang J H, Fan Q, He Z Y. Electronic Structure, Lattice Vibration and Thermoelectric Properties of CuInTe₂[J]. Journal of the chinese ceramic society, 2017, 45(12): 1758-1762.
- [17] Guo S, Zhang A, Li H. Potential 2D thermoelectric material ATeI (A = Sb and Bi) monolayers from a first-principles study[J]. Nanotechnology, 2017, 28(44): 445702.