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DFT Study of Thermoelectric Performance of $SrTiO_3$ Doped by Tantalum

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ABSTRACT

This paper deals with enhancement of thermoelectric performance of $SrTiO_3$ - a perovskite-based material by doping Ti-site with Ta. The electronic and the thermoelectric transport properties of doped $SrTiO_3$ were studied using the first principle calculation in full-potential of density functional theory. Spin-orbit coupling including Hubbard U parameter influences were observed in the investigation. Energy band structure and electron density of state were determined for electronic properties. The Seebeck coefficients, thermal conductivity, electrical conductivity as well as thermoelectric efficiency ZT were calculated for thermoelectric properties. The results of our calculations revealed that narrowing the bandgap of the material leads to the increase of thermoelectric efficiency ZT. At spin-orbit coupling with DFT+U method, ZT of 0.18 at 750 K were obtained and this is similar to the experimental data reported.

Keywords: $SrTiO_3$, Doped, DFT, DFT+U, Spin-Orbit Coupling.

1. INTRODUCTION

The thermoelectric (TE) technique is among several sources of energy conversion. It is a promising approach to convert the waste thermal energies directly into electricity when a temperature gradient is formed on thermoelectric junctions [1-3] and without using harmful chemicals and moving parts [1,2,4]. This temperature difference can be sourced from solar energy, waste heat from home appliances, automobile engine, and even in an industry as heat generated from machines. There are many products in the market that are already using the application of TE such as electronic components [4,5], cooling in diode lasers [6], portable refrigeration [7], and many others. The thermoelectric materials efficiency, called dimensionless figure of merit, can be defined by $ZT = S^2\sigma T/\kappa$; S, σ, κ and T are the Seebeck coefficient, electrical conductivity, thermal conductivity (combination of electronic thermal conductivity and lattice thermal conductivity, i.e. $\kappa = \kappa_e + \kappa_L$) and absolute temperature respectively.

One of the potential n-type oxide is strontium titanate ($SrTiO_3$)[7], a perovskite-based compound. Perovskite oxides offers a wide diversity in terms of composition selection; the A- and B- site cations, as well as oxygen anions, which is flexible in accommodating many elements from the periodic table [8,9]. Many studies have been conducted to enhance the TE efficiency of $SrTiO_3$ (STO) either by doping or changing the processing methods [10,11]. The STO has an n-type nature thermoelectric materials, especially when doped at B-site with Nb element, the

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ZT=0.37 at 1000 K [10,12]. Compared to Nb doping, Ta doping has resulted in the increase of the phonon scattering and at the same time caused the reduction of lattice thermal conductivity. Experimentally, Ta was doped with $SrTiO_3$ and resulted in 0.17 thermoelectric efficiency at 752 K[13].

In this present study, the density functional theory (DFT) method with spin-orbit coupling as well as Hubbard U parameter was adopted in studies of the STO doped with Ta at the B-site. Influence of spin-orbit coupling and U term is taken into account in the electronic and thermoelectric properties of the doped STO. Also, transport properties of thermoelectric materials (Seebeck coefficient, electrical conductivity, thermal conductivity and ZT) were calculated within the temperature range of 250 K and 1200 K. The presence of Ta-doped in STO induced magnetic tendency has been described.

2. COMPUTATIONAL METHODS

The first principle calculation, DFT, is performed using the full-potential linear augmented plane wave and local orbitals (FP-LAPW+lo) method as implemented in WIEN2K package [14]. Calculations in this study were carried out using 60-atoms supercell, which was generated from a five-atom primitive unit cell of STO (space group no. 221, Pm-3m). The percentage of Ta doped in the sample was 8.3%. This was achieved by substitution of 1 Ta atom with Ti out of its 12 atoms present in 60 atoms structure. Similar experimental work reported was 10% of Ta concentration added to STO [13]. In the computation work, four different methods were carried out; standard DFT (no SO, no U), no spin-orbit coupling and DFT+U (no SO,U), spin-orbit coupling and DFT(SO, no U) and spin-orbit coupling and DFT+U(SO, U). The Monkhorst-Pack of 6 × 6 × 4 k-mesh [15] and the generalized gradient approximation were adopted for the exchange-correlation potential to ensure a good convergence of the computed structure and energy. The cutoff energy was defined by $R^{mt}K_{max}$ = 6 with G_{max} = 24. The RMT value (in Angstrom) used for Sr, Ta, Ti, and O were 1.32, 1.05, 1.03 and 0.90 respectively. The energy bound separation between valence electrons and core states is -6 Ry. For the electronic and thermoelectric properties calculations, k-points of 2000 were used. Hubbard U parameter of 0.80 was set for the Ti 3d electrons only.

BoltzTraP code[16] which utilized the semi-classic transport coefficients was used to determine the transport properties of thermoelectric i.e. Seebeck coefficient (S), electrical conductivity (σ/τ), and electronic part of thermal conductivity (k_e/τ). This code interfaces with WIEN2K software. There is a constant relaxation time approximation used in the BoltzTraP code which was based on the Boltzmann transport equation (BTE). The transport tensor can be calculated from the conductivity distributions terms as in Equation 1 and Equation 2:

$$\sigma_{\alpha\beta}(T;\mu) = \frac{1}{\Omega}\int \sigma_{\alpha\beta}(\varepsilon)\left[-\frac{\partial f_\mu(T;\varepsilon)}{\partial\varepsilon}\right]d\varepsilon \quad (1)$$

$$k^{\circ}_{\alpha\beta}(T;\mu) = \frac{1}{e^2T\Omega}\int \sigma_{\alpha\beta}(\varepsilon)(\varepsilon-\mu)^2\left[-\frac{\partial f_\mu(T;\varepsilon)}{\partial\varepsilon}\right]d\varepsilon \quad (2)$$

where κ° is the electronic contributions in the thermal conductivity. The Seebeck coefficients can be calculated from Equation 3:

$$S_{ij} = (\sigma^{-1})_{\alpha i}v_{\alpha j} \quad (3)$$

where ν_α (i,k) is the component of the band velocity. Meanwhile, the band velocity can be calculated from:

$$v_{\alpha\beta}(\mathrm{T};\mu) = \frac{1}{\mathrm{eT}\Omega}\int \sigma_{\alpha\beta}(\varepsilon)(\varepsilon-\mu)\left[-\frac{\partial f_{\mu}(T;\varepsilon)}{\partial\varepsilon}\right]d\varepsilon \quad (4)$$

where fμ, is the Fermi distribution function, μ = E_F is the Fermi energy, e is the charge of the electron, T is temperature and Ω is the volume. In this case, relaxation time was assumed as an energy independent team. Therefore, temperature and doping level would not be influenced.

3. RESULTS AND DISCUSSION

The electronic and thermoelectric properties of STO compound doped with Ta element at B-site were analysis in subsections below.

3.1 Electronic Properties

Crystallizes structure of $SrTi_{0.916}Ta_{0.083}O_3$ was found to be a cubic structure with Pm3m space group. The optimized lattice parameter of the doped compound; $SrTi_{0.916}Ta_{0.083}O_3$ was 3.945Å, which is similar to pure STO of 3.944Å. This is as a result of a small percentage of doping. In Fig. 1, the calculated band structures are shown with the direct energy band gap at the Γ point. By comparing the electronic band structures obtained, all the band gap result is 1.77 eV except SO, U method which is 2.35 eV. That is a result of Hubbard U-parameter is presented in the calculation. The Hubbard U parameter was used to improve the underestimated results of DFT in band structure calculation [17,18]. The E_F was set at zero of the energy in band structure plotted. Conduction band (CB) shifting shows the semi-metal behaviour of the material in the present of Ta doped. Furthermore, the position of E_F at CB showing the presence of frees electrons within the region. Thus, there is an n-type electrical conductivity nature in the material. The spin-orbit coupling and Hubbard U-parameter influence do not show on the physical band structure, except the narrowing of band gap which was caused by U parameter as mentioned earlier. The total magnetic moment calculated was 0.518 μ_B, generated majorly from Ti-3d and Ta-5d, during SO calculations i.e 'SO, U' and 'SO, no U' methods. All DOS states near E_F were mainly due to the Ti-3d and Ta-5d orbitals.

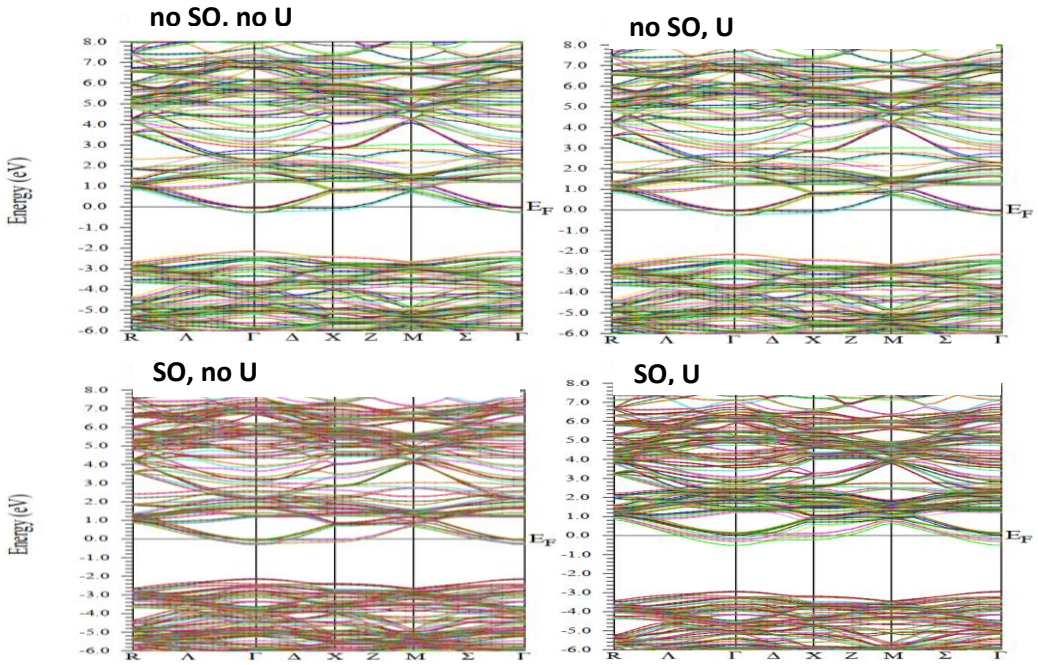

Figure 1. Band structure of $SrTi_{0.916}Ta_{0.083}O_3$ compound, at different methods of calculations, along the symmetry line of the Brillouin zone. The energy scale is in atomic units and the Fermi energy level was set at zero.

To illustrate the band structures influence due to Ta doping, this study investigated the total and partial electron density of states (TDOS and PDOS), as shown in Fig. 2 and Fig. 3. It was observed that the peak of the valence band (VB) was composed mainly of the O-2p orbital as well as a minor influence from Ti-3d, and Ta-5d orbitals. The lower conduction band (CB) was generated mostly by the Ti-3d, Ta-5d orbitals and a little influence of the O-2p and Sr-3d orbitals.

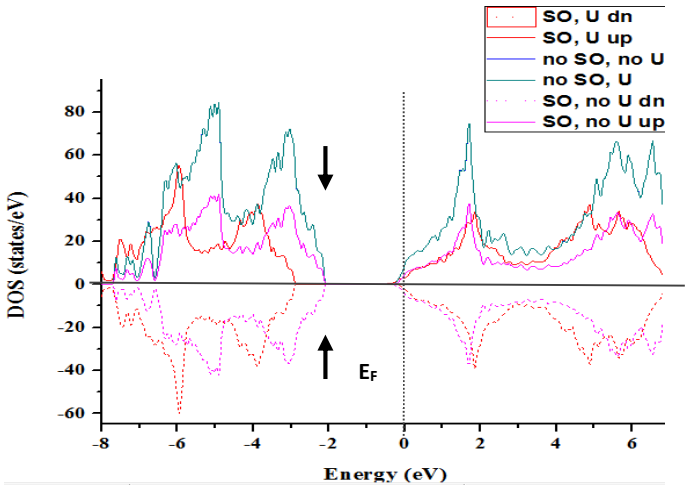

Figure 2. Density of state of $SrTi_{0.916}Ta_{0.083}O_3$.

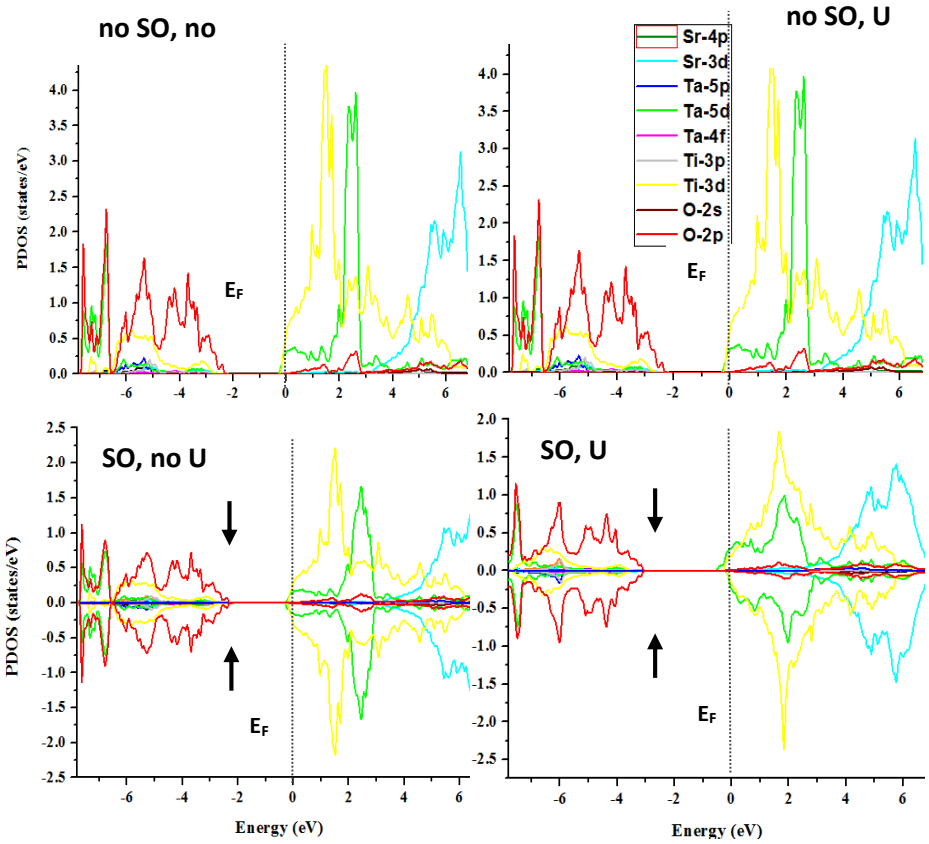

Figure 3. Partial density of state of $SrTi_{0.916}Ta_{0.083}O_3$.

3.2 Thermoelectric Properties

The thermoelectric properties were calculated using BoltzTraP program as implemented in WIEN2k package [16]. The temperature dependence of electrical conductivity (σ/τ), Seebeck coefficient (S), electronic part of thermal conductivity (κ_e/τ) and figure of merit ZT were plotted for all methods, where τ is the relaxation time.

Figure 4a shows the Seebeck coefficient (S) of the sample via different methods as a function of temperature. Negative S value across the whole temperature range was observed, which also shows the n-type conduction, proving that electrons are the majority carriers when doped Ta on STO. The S has almost the same value -40 μV/K to -118 μV/K at a temperature of 250 to 1200 K for all methods expect 'SO, U' method which is -23 μV/K to -103 μV/K at the same temperature range. Thus, this can also be attributed to higher carrier density of Ta in STO when using DFT+U with SO. The absolute value of S increases with an increase in temperature, which is due to the low concentration of charge carriers [19].

Electrical conductivity (σ/τ) of doped Ta in STO was plotted against temperature as shown in Figure 4b. The σ/τ increases monotonically with temperature, which result from excess electrons flow, which follows the general behaviour of the semiconductor. In SO, U method the σ/τ value is much less compared to other methods, as a result of low electron density of state at Fermi level. For comparison, Upadhyay Kahaly and Schwingenschlogl, reported a similar trend for $Sr_{0.917}Pr_{0.083}TiO_3$[20].

The electronic part of thermal conductivity (k_e/τ) can only be calculated from BoltzTraP code [16]. Figure 4c depicts the variation of k_e/τ with the temperature. The value of k_e increases as temperature increasing in all methods. The k_e/τ of 0.32×10^{15} Wm/Ks were recorded for SO, U method at room temperature which is good for thermoelectric material of $Sr_{0.917}Ta_{0.083}TiO_3$. Figure 4d shows the temperature dependence of the dimensionless figure of merit (ZT). The ZT value increases as temperature changed. The computation results of SO, U method show that ZT at 750 K for $Sr_{0.917}Ta_{0.083}TiO_3$ is 0.18. This is similar to the experimental result of $Sr_{0.90}Ta_{0.10}TiO_3$ compound at almost the same temperature range.

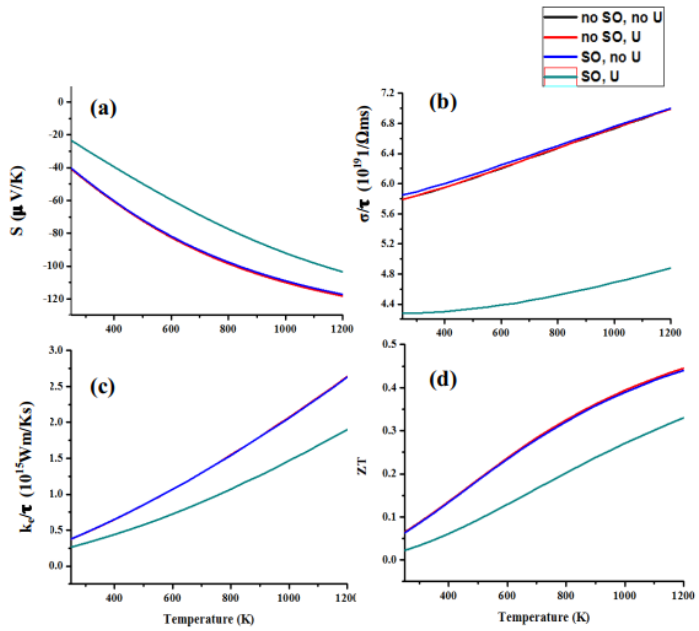

Figure 4. Influence of the Hubbard U (U) parameter and spin–orbit (SO) coupling on the thermoelectric properties: (a) Seebeck coefficient, (b) electrical conductivity, (c) thermal conductivity, and (d) dimensionless figure of merit of $SrTi_{0.917}Ta_{0.083}O_3$.

4. CONCLUSIONS

Influence of 8% of Ta as a dopant in $SrTiO_3$ at the Ti site has been studied using first principle calculations as implemented in the WIEN2k code. The electronic and thermoelectric properties were investigated. The spin-polarized calculation indicates magnetism of $SrTiO_3$ at 8% of Ta doped. It was observed that an enhancement of the density of states near E_F leads to higher Seebeck coefficient in spin-polarized calculation with Hubbard U. At the same time, the band gap result was improved. In the thermoelectric studies, it was found that thermal and electrical conductivities, and even absolute Seebeck coefficient increases with the increment of temperature. This study obtained ZT =0.18 (at 750 K) when using SO, U method, which was very close to the experimental report. The maximum figure of merit of 0.33 was obtained at 1200 K for $Sr_{0.917}Ta_{0.083}TiO_3$ using the same method.

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REFERENCES

[1] O. Afshar, R. Saidur, M. Hasanuzzaman & M. Jameel, "A review of thermodynamics and heat transfer in solar refrigeration system," Renewable and Sustainable Energy Reviews, **16**, 8 (2012) 5639-5648.

[2] J. Yang, H. L. Yip & A. K. Y. Jen, "Rational design of advanced thermoelectric materials,"Advanced Energy Materials **3**, 5 (2013) 549-565.

[3] N. Kalkan, E. A. Young & A. Celiktas, "Solar thermal air conditioning technology reducing the footprint of solar thermal air conditioning". Renewable and Sustainable Energy Reviews **16**, 8 (2012) 6352-6383.

[4] H. Alam & S. Ramakrishna, "A review on the enhancement of figure of merit from bulk to nano-thermoelectric materials," Nano energy, **2**, 2 (2013) 190-212.

[5] Z. L. Wang, T. Onda & Z. C. Chen, "Effect of Cu doping on microstructure and thermoelectric properties of Bi2Te2. 85Se0. 15 bulk materials". Scripta Materialia, **146**, (2018) 119-122.

[6] R. N. Abed, "The Thermal Management System of Laser Diode. A Review," ARPN Journal of Engineering and Applied Sciences **5260**, 10-12 (2015) 5250.

[7] R. M. Atta, "Solar thermoelectric cooling using closed loop heat exchangers with macro channels," Heat and Mass Transfer **53**, 7 (2017) 2241-2254.

[8] C. Gayner & K. K. Kar, "Recent advances in thermoelectric materials," Progress in Materials Science **83** (2016) 330-382.

[9] N. F. Atta, A. Galal & H. Ekram, H. "Perovskite nanomaterials–synthesis, characterization, and applications," In Perovskite Materials-Synthesis, Characterisation, Properties, and Applications. IntechOpen, (2016).

[10] I. Mahmud, M. S. Yoon, I. H. Kim, M. K. Choi & S. C. Ur, "Thermoelectric properties of the ceramic oxide Sr 1− x La x TiO 3," Journal of the Korean Physical Society **68**, 1 (2016) 35-40.

[11] P. P. Shang, B. P. Zhang, Y. Liu, J. F. Li & H. M. Zhu, "Preparation and thermoelectric properties of la-doped SrTiO 3 ceramics," Journal of electronic materials **40**, 5 (2011) 926-931.

[12] M. Saxena, K. Tanwar & T. Maiti, "Environmental friendly Sr2TiMoO6 double perovskite for high temperature thermoelectric applications," Scripta Materialia **130** (2017) 205-209.
[13] Y. Cui, J. R. Salvador, J. Yang, H. Wang, G. Amow & H. Kleinke, "Thermoelectric properties of heavily doped n-type SrTiO 3 bulk materials," Journal of electronic materials **38**, 7 (2009) 1002-1007.
[14] P. Blaha, K. Schwarz, G. K. Madsen, D. Kvasnicka & J. Luitz, "WIEN2k: An Augmented Plane Wave Plus Local Orbital Program for Calculating Crystal Properties Tech," University Vienna, (2001).
[15] H. J. Monkhorst & J. D. Pack, "Special points for Brillouin-zone integrations," Physical review B, **13**, 12(1976) 5188.
[16] G. K. Madsen & D. J. Singh, "BoltzTraP. A code for calculating band-structure dependent quantities," Computer Physics Communications **175**, 1 (2006) 67-71.
[17] B. Himmetoglu, A. Floris, S. De Gironcoli & M. Cococcioni, "Hubbard-corrected DFT energy functionals: The LDA+ U description of correlated systems," International Journal of Quantum Chemistry **114**, 1 (2014) 14-49.
[18] N. Hernández-Haro, J. Ortega-Castro, Y. B. Martynov, R. G. Nazmitdinov & A. Frontera, A. "DFT prediction of band gap in organic-inorganic metal halide perovskites: An exchange-correlation functional benchmark study," Chemical Physics **516** (2019) 225-231.
[19] A. V. Kovalevsky, A. A. Yaremchenko, S. Populoh, A. Weidenkaff & J. R. Frade, "Enhancement of thermoelectric performance in strontium titanate by praseodymium substitution," Journal of Applied Physics **113**, 5 (2013) 053704.
[20] M. U. Kahaly & U. Schwingenschlögl, U. "Thermoelectric performance enhancement of SrTiO 3 by Pr doping," Journal of Materials Chemistry A **2**, 27 (2014) 10379-1038.