International Journal of Nanoelectronics and Materials

In Press, Accepted Manuscript – Note to user

DFT study of Thermoelectric Performance of $SrTiO_3$ doped by Tantalum.

Akeem Adekunle Adewale[1,2*], Abdullah Chik[1], Ruhiyuddin Mohd Zaki[1], Faizul Che Pa[1], Yeoh Cheow Keat[1], and Noorina Hidayu Jamil[1]

[1]School of Materials Engineering, Universiti Malaysia Perlis (UniMAP), 02600 Arau, Jejawi, Perlis, Malaysia.

[2] Physics and Materials Science Department, Kwara State University, Malete, Kwara, Nigeria.

[*]Corresponding author; getcutica@gmail.com

Abstract

This paper deals with the enhancements 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 was observed in the investigation. Energy band structure and electron density of state are determined for electronic properties while 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 the 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 had an n-type nature thermoelectric materials,

especially when doped at B-site with Nb element, the ZT=0.37 at 1000 K [10,12]. Since Ta doping compared with Nb doping has resulted in the increase of the phonon scattering and at the same time caused the reduction of lattice thermal conductivity. Experimentally, Ta had 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 principles calculation, DFT, are performed using the full-potential linear augmented plane wave and local orbitals (FP-LAPW+lo) method as implemented in WIEN2K package[14]. Our calculations were carried out with 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 were define through $R^{mt}K_{max} = 6$ 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 0.60 was set for the Ti 3d electrons only.

BoltzTraP code[16] which utilized the semi-classic transport coefficients, used to determine the transport properties of thermoelectric; Seebeck coefficient (S), electric conductivity (σ/τ), and electronic part of thermal conductivity (k_e/τ). This code is interfaces with WIEN2K software. There is 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

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

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

where κ° is the electronic contributions in the thermal conductivity. The Seebeck coefficients can be calculated from the expression below;

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

where v_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 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 were 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 was a result of Hubbard U-parameter present 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 behavour 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 earlier mention. The total magnetic moment of calculated is 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 are mainly due to the Ti-3d and Ta-5d orbitals.

To illustrate the band structures influence due to Ta doping, we investigated the total and partial electron density of states (TDOS and PDOS), as shown in Fig. 2 and 3. We 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.

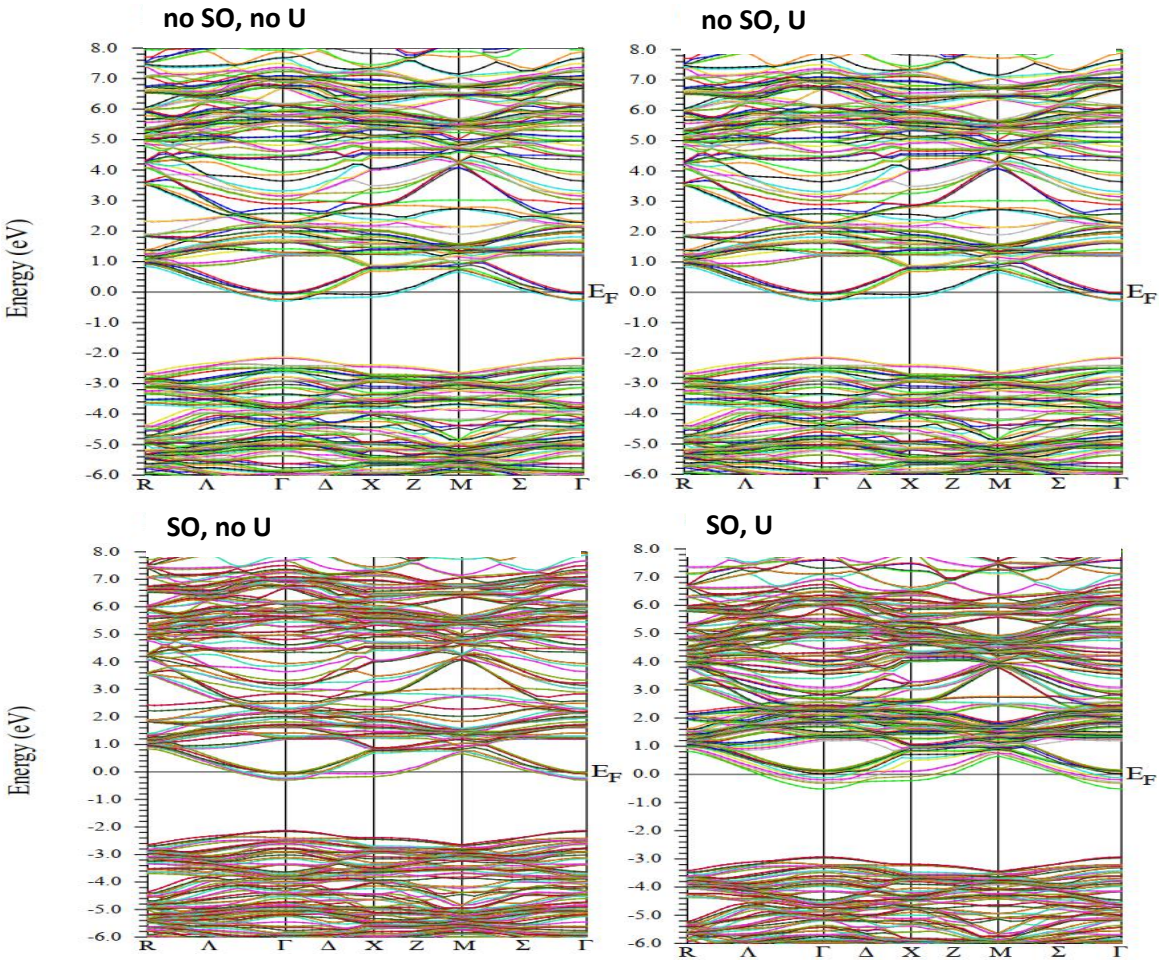

Figure 1: Band structure of $SrTi_{0.916}Ta_{0.083}O_3$ compound, at different methods of calculations, along the symmetry line of the Brillouin zone. The energy scale is in atomic units and the Fermi energy level was set at zero.

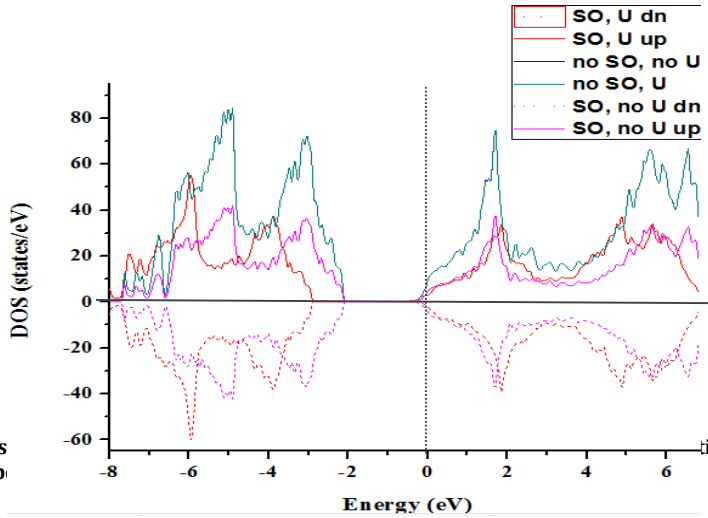

Figure 2: Density of state of $SrTi_{0.916}Ta_{0.083}O_3$.

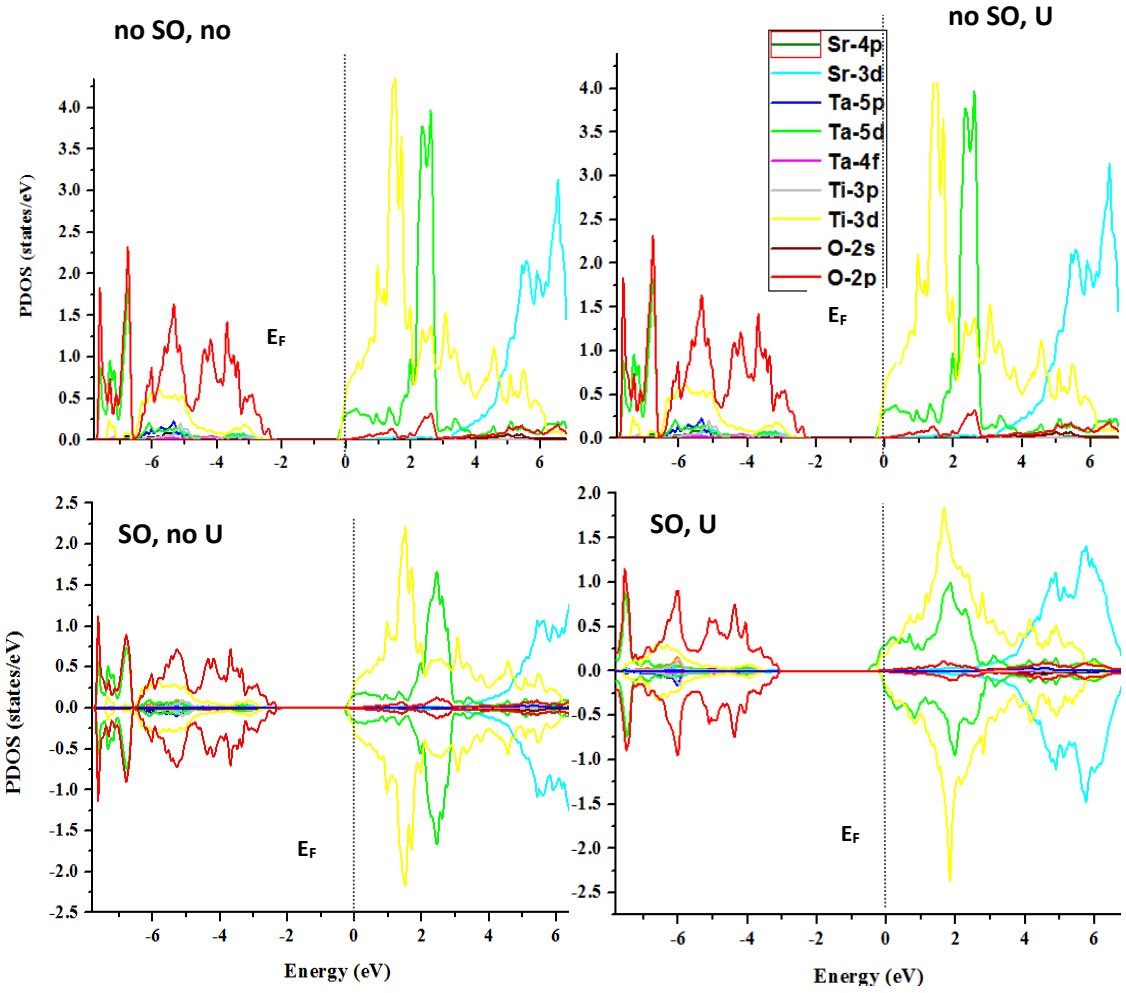

Figure 3: Partial density of state of $SrTi_{0.916}Ta_{0.083}O_3$.

3.2 Thermoelectric properties

We calculated the thermoelectric properties 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 are 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 that 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 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].

Note electronic part of thermal conductivity (k_e/τ) can only be calculated by 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 increased as temperature change. 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.

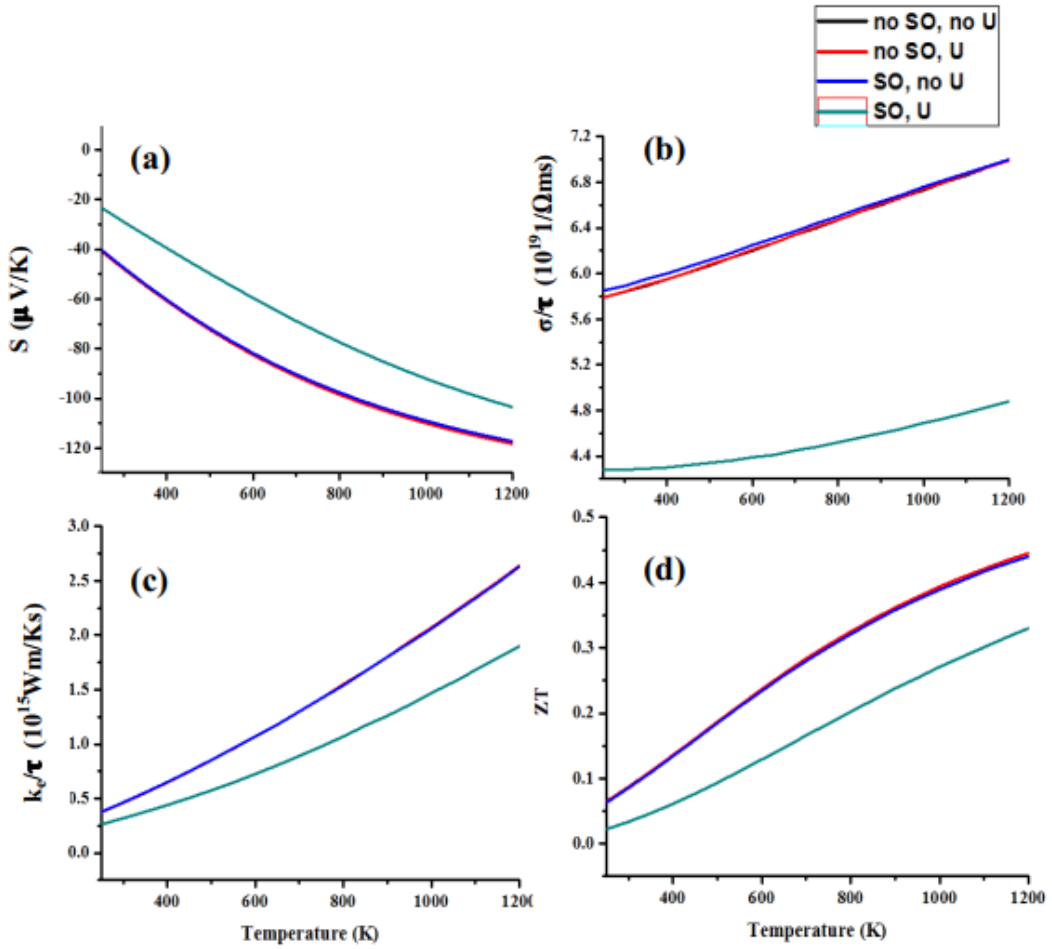

Figure 4: shows the influence of the Hubbard U (U) parameter and spin–orbit (SO) coupling on the thermoelectric properties: (a) Seebeck coefficient, (b) electrical conductivity, (c) thermal conductivity, and (d) dimensionless figure of merit of $SrTi_{0.917}Ta_{0.083}O_3$.

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 implement in WIEN2k code. The electronic and thermoelectric properties are investigated. The spin-polarized calculation indicates none magnetism of $SrTiO_3$ at 8% of Ta doped. We observed 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 improved band gap result. In our thermoelectric studies, we found that thermal and electrical conductivities, and even absolute Seebeck coefficient increases with increase in temperature. We obtained ZT =0.18 (at 750 K) when using SO, U method which is very close to the experimental report. The maximum figure of merit of 0.33 was obtained at 1200 K for $Sr_{0.917}Ta_{0.083}TiO_3$ with the same method.

Acknowledgments

The authors would like to extend their appreciation to Centre for Frontier Materials Research, Center of Excellence Geopolymer & Green Technology (CEGeoGTech) and the School of Materials Engineering, Universiti Malaysia Perlis. Also, we thank the Malaysian Government for their financial support of this project through the Fundamental Research Grant Scheme (FRGS/1/2016/STG07/UNIMAP/02/3).

References

[1] O. Afshar, R. Saidur, M. Hasanuzzaman and M. Jameel, "A review of thermodynamics and heat transfer in solar refrigeration system," *Renewable and Sustainable Energy Reviews*, vol. 16, no. 8, pp. 5639-5648, 2012.

[2] J. Yang, H. L. Yip and A. K. Y. Jen, "Rational design of advanced thermoelectric materials,"*Advanced Energy Materials*, vol. 3, no. 5, pp. 549-565, 2013.

[3] N. Kalkan, E. A. Young and A. Celiktas, "Solar thermal air conditioning technology reducing the footprint of solar thermal air conditioning". *Renewable and Sustainable Energy Reviews*, vol. 16, no. 8, pp. 6352-6383, 2012

[4] H. Alam and S. Ramakrishna, "A review on the enhancement of figure of merit from bulk to nano-thermoelectric materials," *Nano energy*, vol. 2, no. 2, 190-212, 2013.

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

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

[7] R. M. Atta, "Solar thermoelectric cooling using closed loop heat exchangers with macro channels," *Heat and Mass Transfer*, vol. 53, no.7, pp. 2241-2254, 2017.

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

[9] N. F. Atta, A. Galal and 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, and S. C. Ur, "Thermoelectric properties of the ceramic oxide Sr 1− x La x TiO 3," *Journal of the Korean Physical Society*, vol. 68, no. 1, pp. 35-40, 2016.

[11] P. P. Shang, B. P. Zhang, Y. Liu, J. F. Li and H. M. Zhu, "Preparation and thermoelectric properties of la-doped SrTiO 3 ceramics," *Journal of electronic materials*, vol. 40, no. 5, pp. 926-931, 2011.

[12] M. Saxena, K. Tanwar and T. Maiti, "Environmental friendly Sr2TiMoO6 double perovskite for high temperature thermoelectric applications," *Scripta Materialia*, vol. 130, pp. 205-209, 2017.

[13] Y. Cui, J. R. Salvador, J. Yang, H. Wang, G. Amow and H. Kleinke, "Thermoelectric properties of heavily doped n-type SrTiO 3 bulk materials," *Journal of electronic materials*, vol. 38, no. 7, pp. 1002-1007, 2009.

[14] P. Blaha, K. Schwarz, G. K. Madsen, D. Kvasnicka and J. Luitz, "WIEN2k: An Augmented Plane Wave plus Local Orbital Program for Calculating Crystal Properties Tech," *University Vienna*, 2001

[15] H. J. Monkhorst and J. D. Pack, "Special points for Brillouin-zone integrations," *Physical review B*, vol. 13, no. 12, pp. 5188, 1976.

[16] G. K. Madsen and D. J. Singh, "BoltzTraP. A code for calculating band-structure dependent quantities," *Computer Physics Communications*, vol. 175, no. 1, pp. 67-71, 2006.

[17] B. Himmetoglu, A. Floris, S. De Gironcoli and M. Cococcioni, "Hubbard-corrected DFT energy functionals: The LDA+ U description of correlated systems," *International Journal of Quantum Chemistry*, vol. 114, no.1, pp. 14-49, 2014.

[18] N. Hernández-Haro, J. Ortega-Castro, Y. B. Martynov, R. G. Nazmitdinov and A. Frontera, A. "DFT prediction of band gap in organic-inorganic metal halide perovskites: An exchange-correlation functional benchmark study," *Chemical Physics*, vol. 516, pp. 225-231, 2019

[19] A. V. Kovalevsky, A. A. Yaremchenko, S. Populoh, A. Weidenkaff and J. R. Frade, "Enhancement of thermoelectric performance in strontium titanate by praseodymium substitution," *Journal of Applied Physics*, vol. 113, no. 5, pp. 053704, 2013.

[20] M. U. Kahaly and U. Schwingenschlögl, U. "Thermoelectric performance enhancement of SrTiO 3 by Pr doping," *Journal of Materials Chemistry A*, vol. 2, no. 27, pp. 10379-1038, 2014