Structural, electronic and thermoelectric properties of SrTiO3 ceramic doped by lanthanum using first principles

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Abstract. The Sr0.92La0.08TiO3 model compound was studied by means of the first-principles method grounded on the full-potential linearized augmented plane wave with the local orbital method as implement in WIEN2k. The structures, electronic and thermoelectric properties of the model compound are examined. Geometry optimization of Sr0.92La0.08TiO3 compound structure reveals the lattice constant of 3.9451 Å, which is the same as un-doped SrTiO3. The direct bandgap of 2.48 eV (Γ-Γ) was measured from computed electronic band structure and its displayed density of states for Sr0.92La0.08TiO3 sample. Transport properties were calculated using BoltzTraP code as implemented in the WIEN2k code. The results were analyzed as a function of the variable temperatures, the density of state and chemical potential. Temperature and density of state variation with transport properties are in the same trend. Chemical potential proves material as n-type via Seebeck coefficient. The thermoelectric performance ZT of 0.05 was obtained at room temperature, while maximum value of 3.79 was recorded at 1200 K.

1 Introduction

Thermoelectric (TE) devices convert waste thermal energy to electrical energy through the Seebeck effect principle and vice versa by the Peltier effect [1]. This conversion has been used for many applications in solid-state power generation and cooling [2-5]. The conversion efficiency of thermoelectric materials is related to dimensionless figure of merit (ZT) and it is expressed as [6]; ZT = (S^2/ρk)T, where S is thermopower (Seebeck coefficient), ρ is electrical resistivity, k is thermal conductivity and T is temperature. The k is the summation of; lattice thermal conductivity k_latt and electrical thermal conductivity k_e. Strontium titanate (SrTiO3) is a transition metal oxide that has attracted significant attention as alternative thermoelectric (TE) material due to its potentials such as less toxicity, high temperature

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resistance, etc. It is an n-type semiconductor with high Seebeck coefficient (~850 μV K\(^{-1}\)), low electrical conductivity and high thermal conductivity (6 Wm/K) at room temperature [7,8]. Hence, the thermoelectric performance of undoped SrTiO\(_3\) is low due to high thermal conductivity with a low electrical conductivity that emanates from the wide band-gap insulator. There are many approaches to improve the properties of SrTiO\(_3\) such as doping, oxygen vacancy and many others.

Generally, the addition of impurity to thermoelectric materials has successfully enhanced the ZT value by reducing the thermal conductivity while conserving the electrical conductivity and thermopower [9-11]. The high power factor of 28 – 36 μWcm\(^{-1}\)K\(^{-2}\) had been obtained by the La-doped SrTiO\(_3\) compound at room temperature [12] which is similar to state-of-art material Bi\(_2\)Te\(_3\) compounds [3]. Likewise, a large Seebeck coefficient similar to that of Bi\(_2\)Te\(_3\) was described by Okuda et al., 2001 for Sr\(_{1-x}\)La\(_x\)TiO\(_3\) (0 ≤ x ≤ 1) [12]. The pentavalent impurity in SrTiO\(_3\) with higher valence ions on Sr- or Ti-site and by oxygen vacancies [13-17], gives ZT values at range of 0.36 - 0.41 for single doping between temperature of 970 K and 1100 K[10,20,21]. In case of co-doping on A- and B-sites of ABO\(_3\) perovskite compound using La- and Nb- atoms respectively, ZT value > 0.6 at a temperature above 1000 K was reported [16]. In this present study, first principle approach based on density functional theory within PBE-GGA approximation [20] was used as implemented in WIEN2k code. Structural and electronic properties of pure SrTiO\(_3\) and La-doped SrTiO\(_3\) were investigated. Thermoelectric transport properties of Sr\(_{0.92}\)La\(_{0.08}\)TiO\(_3\) compound were calculated using BoltzTraP code [21]. The transport results were analyzed with their influence on temperature, the density of states and chemical potential.

2 Methods of calculation

The first-principles calculation was used to investigate the Sr\(_{0.92}\)La\(_{0.08}\)TiO\(_3\) compound based on WIEN2k code [22]. Full potential linearized augmented plane wave plus local orbital method within density functional theory (DFT) calculation was performed including spin-orbit coupling. An exchange-correlation function Perdew-Burke Ernzerh (PBE) of generalized gradient approximation (GGA) [20] is adopted for calculation of total ground state energy as well for optimizing of the structural cells internal parameters. The kinetic energy cutoff K\(_{\text{max}}\) = 6/RMT was used for the plane-wave basis set during energy convergence. Muffin-tin radii (RMT) were set as 2.5 a.u for Sr and La atoms, 1.95 and 1.76 a.u for Ti and O atoms respectively. The maximum value for waves function within muffin-tin of the atomic sphere is l\(_{\text{max}}\) = 12, while the charge density is Fourier expanded up to G\(_{\text{max}}\) = 24 (a.u.). In self-consistent calculations, the total energy and charge convergence norms were set to 10\(^{-4}\) Ry and 0.001e, respectively. The core states and valence states separation energy was fixed to -6.0 Ry.

On-site electronic interaction Hubbard U of 0.8 eV was set for all calculations with the exchange parameter (J = 0). Based on the use of localized basis sets the U value was imposed on d state of Ti atom [23]. The Monkhorst-Pack’s [24] k-points grid of 6\(^{\times}\)6\(^{\times}\)4 is used in the irreducible Brillouin zone (IBZ) for electronic structure calculations. Geometry optimization of the study compound was performed using the equation of state by Birch-Murnaghan’s [25]. The thermoelectric transport properties were calculated using semi-classical Boltzmann transport equation as applied in BoltzTraP code [21]. A high dense k-point of 14\(^{\times}\)14\(^{\times}\)9 is used for transport calculation. Calculations are performed from temperature of 300 K to 1200 K. For a variation of the thermoelectric (TE) properties and temperature, TE results at the chemical potential of 0 K Fermi energy were used for plots. Likewise, TE values were plotted against the chemical potential of range -2 to 2 eV and as well as DOS (182 – 207 states/eV), in order to investigate the effects of DOS and chemical potential on thermoelectric properties.
3 Results and discussion

3.1 Structural properties

Structural optimization of the $\text{Sr}_{0.92}\text{La}_{0.08}\text{TiO}_3$ compound was carried out using the equation of state as earlier said in section 2. This is carried out by fitting the total energy of the unit cell against the volume. The optimized calculated structural parameters are in good agreement with other available computational works as displayed in Table 1. Distortion was not observed in the lattice constant as a result of the small percentage of La in the whole supercell. Figure 1 shows the variation in energy against change in volume during the structural optimized calculation. The bond lengths of computed compounds are measured using XCrysDen tool [26] and displayed in Table 2, the results are compared to available DFT work[27]. The calculated bond length is used to evaluate tolerance factors ($t$) that can be used to determine the stability of perovskite compound phase transition [28].

$$t = \frac{0.707(A-O)}{(B-O)}$$

where A-O and B-O are the compound bond length from A site to O atom and B site to O atom respectively. The $\text{Sr}_{0.92}\text{La}_{0.08}\text{TiO}_3$ compound is still maintaining cubic structure with space group number (Pm3m) since its 't' value is 1.00 which is in the range of 0.93-1.02 for cubic perovskite compound. In Figure 2, the crystal structure of the study compounds are shown. The La atom is substituted for one of 12 Sr - atoms in the supercell, surrounded by four TiO$_6$ octahedral. So, La/ Sr is coordinated by 12 O - atom. The Ti - atom is in six-fold coordinated by O – atom.

![Fig. 1. Changes in energy against volume for SrTiO$_3$ and Sr$_{0.92}$La$_{0.08}$TiO$_3$ compounds.](image-url)
Table 1. Optimized lattice parameter, volume, bulk modulus and bulk modulus derivative (B’).

| Samples          | Lattice constant (Å) | Volume (Å³) | Bulk modulus (GPa) | Derivative bulk modulus | Ref.  |
|------------------|----------------------|-------------|-------------------|-------------------------|-------|
| SrTiO₃           | 3.9451               | 735.84      | 189.17            | 6.62                    | Present work |
| Sr₉₀.₉₂La₀.₀₈TiO₃| 3.9451               | 737.42      | 195.23            | 7.33                    | Present work |
| SrTiO₂           | 3.9125               | 173.71      |                   | 7.33                    | [29]   |
|                  | 3.9400               | 169.51      |                   |                         | [27]   |

Table 2. Measured bond length for study compounds.

| Samples          | Bond length | Present work | Other computational work[27] | Tolerance factors (t) |
|------------------|-------------|--------------|------------------------------|-----------------------|
| SrTiO₃           | A-O         | 2.7896       | 2.79                         | 1.00                  |
|                  | A-B         | 3.4166       | 3.41                         |                       |
|                  | B-O         | 1.9726       | 1.97                         |                       |
| Sr₉₀.₉₂La₀.₀₈TiO₃| A-O         | 2.7896       |                              | 1.00                  |
|                  | A-B         | 3.4166       |                              |                       |
|                  | B-O         | 1.9726       |                              |                       |

Fig. 2. Crystal structures of SrTiO₃ and Sr₉₀.₉₂La₀.₀₈TiO₃ compound, where the four kinds of atoms are distinguished by coloured spheres as Sr (cyan), La (blue), Ti (gray) and O (red).

3.2 Electronic properties

The computed band structure and density of the state of the study compound are shown in Figures 2 and 3. The band structures were plotted along symmetry points; R(0.5 0.5 0.5); Γ(0.0 0.0 0.0); X(0.0 0.5 0.0); M(0.5 0.5 0.0) and Γ(0.0 0.0 0.0) of the Brillouin zone as demonstrated in Figure 3. Possible electron transition can be investigated through the
conduction and valence bands of the band structure. We obtained 3.26 eV bandgap in SrTiO$_3$ compound with the Hubbard U in DFT+U calculation. This is similar to the experimentally reported band gap of 3.25 eV[30]. SrTiO$_3$ band structure confirmed the semiconducting nature of the compound with the position of Fermi energy level (E$_F$) at the edge of the valence band (VB). The model compound Sr$_{0.92}$La$_{0.08}$TiO$_3$ displayed semi-metallic behavior as a result of overlapping E$_F$ on the conduction band (CB). This caused the material to become an electron charge carrier (n-type). The direct bandgap (2.48 eV) was measured from CB minimum and VB maximum of the compound at Γ-Γ points of IBZ. The direct energy band is consistent with the previous study on SrTiO$_3$ band structure [31]. The presence of La doping shrinks the bandgap of Sr$_{0.92}$La$_{0.08}$TiO$_3$ compound [32,33].

Fig. 3. Electron band structure for SrTiO$_3$ and Sr$_{0.92}$La$_{0.08}$TiO$_3$ compounds.

The contributions of each atom in band structure lines cluster were analyzed by computing total and partial density of state (TDOS and PDOS). TDOS and PDOS can be divided into two energy regions; conduction and valence. For SrTiO$_3$ compound, three prominent peaks of the electron were observed in TDOS; one from the conduction band and two from the valence band. PDOS of SrTiO$_3$ (Figure 4) shows that 2p state of O-atom and 3d state of Ti atom dominated at VB and CB respectively. This is similar to other simulation work on SrTiO$_3$[27,31]. A non-magnetic behavior was confirmed with identical spin up and spins down of DOS orbitals. In Sr$_{0.92}$La$_{0.08}$TiO$_3$ compounds, the conduction band composed of 3d state of Ti and Sr atoms with the 5d state of La. Each atom established its participation with a peak of an electron as shown in Figure 4. The VB is dominated by 2p state of O atom at both spin and the same time they are symmetry. In Figure 4, the semi-metallic behavior of the Sr$_{0.92}$La$_{0.08}$TiO$_3$ compound was confirmed by spin-up TDOS exhibiting metallic and spin-down displayed semiconducting nature. It is noticed that La substitution in SrTiO$_3$ leads to metallic nature [34] in the spin-up region.
3.3 Thermoelectric properties

Our transport properties calculation is based solely on compounds Sr$_{0.92}$La$_{0.08}$TiO$_3$. Thermopower, electrical conductivity, and electronic thermal conductivity are calculated in terms of temperature, the density of state, and chemical potential ($\mu$) as shown in Figure 5-6. Figure 5 demonstrates the chemical potential dependence of parameters of transport at 1000 K. Contrary to the current potential repulsive force, the chemical potential indicates the energy need to insert an electron in the process. The sign of potential chemical value shows semiconducting regions of type n (negative) and type p (positive) [35].

![Variation of chemical potential with thermoelectric properties for Sr$_{0.92}$La$_{0.08}$TiO$_3$ compounds.](image-url)
A high Seebeck coefficient value of 947.72μVK⁻¹ is recorded for μ of -1.69 eV, a negative value confirms the material's n-type existence as previously reported in the electronic properties analysis. A positive value of chemical potential, electrical conductivity and electronic thermal conductivity are increased. Electrical conductivity is directly proportional to chemical potential (μ) as calculated by relationship [5]: σ = neμ, where n is concentration of carrier and μ is mobility of carrier. Clearly, ZT of the study compound is record high value of ~1.25 at the chemical potential from -0.67 eV to -0.61 eV.

The temperature and DOS dependent on Seebeck coefficient were plotted in Figure 6 (a & b). The negative value of S indicates that major carriers are electrons. This confirmed the position of EF in the band structure and density of state. The absolute S value increase in both cases. A negative value of S value can be attributed to La –atom impurity in the compound with shifting of EF to CB region in the band structure. The S value at 1200 K is -107.59 μVK⁻¹. A large value of DOS (206.6 eV) is responsible for such a high Seebeck coefficient. The electrical conductivity (σ/t) increases with the temperature / DOS as shown in Fig. 6(c & d). This indicates the semiconducting nature of the compound; this confirms the DOS analysis (at spin down region) in electronic properties. Also with increasing temperature, the electrons get sufficient energy to cross the energy barrier at Fermi-level and therefore increasing electrical conductivity [36]. Since chemical potential is subjected to the temperature by the relation; μ ∝ √T⁻³[37]. Electrical conductivity increases due to chemical potential increasing with temperature. The σ/t increased from 3.52×10¹¹ Sm.s⁻¹ at room temperature to 4.23 ×10¹¹ Sm.s⁻¹ at 1200 K.

The thermal conductivity k consists of the electron part ke and the lattice vibration (phonon) part kl, as k= ke + kl. Only ke/τ can be determined from BoltzTraP code [21,29]. The electronic thermal conductivity has been shown in Figure 6(e&f) to vary with temperature / DOS. With an increase in temperature / DOS, the measured ke/τ increases monotonically. For temperature changing we recorded 2.75×10¹⁴ Wm/Ks of ke/τ at 300 K and 15.49×10¹⁴ Wm/Ks at 1200 K. This can be due to the effect of electronic thermal conductivity, since with the increase in temperature, the charge carriers are heat excited, as a result, the ke increasing [37].

In Figure 6(g & h), the dependent of the dimensionless figure of merit (ZT) on temperature/ DOS is present. The calculated ZT value increased with the increase in temperature which is the same trend with experimental work [38]. The ZT value can be attributed to the large value of S and higher ke/τ at the same time. At the temperature of 300 K, ZT of 0.05 was recorded and at a higher temperature of 1200 K, it was 0.39. This result is similar to many experimental reports ~0.37 of ZT value at 973 K for 9.0 % La doping [38] and ZT of 0.28 at 773 K in Lₐ₀.₁₂S₁₀.₈₇TiO₃[39].
4 Conclusion

Density functional theory calculation was implemented to study the structural, electronic and thermoelectric properties of $\text{Sr}_{0.92}\text{La}_{0.08}\text{TiO}_3$. Semi-classical Boltzmann transport equation was solved for thermoelectric transport properties using BoltzTraP code. The cubic structure of the doped compound, similar to un-doped, was obtained after structural optimization using the equation of state by Birch-Murnaghan’s. During electronic properties analyses with band structure and density of states, the energy band gap of 2.48 eV was obtained which was attributed to La atom present in the compound. The spin-down of DOS reveals semiconducting nature and spin up shows the metallic behaviour. This was combining in the band structure plots as semi-metallic with the Fermi level partial crossing of the conduction bands. Thermoelectric properties were analyzed by plotting the variation of transport properties with chemical potential, temperature, and density of states. In chemical potential variation with transport properties, large negative Seebeck coefficient value was recorded show the n-type nature of compound by S. Temperature and DOS displayed the same trends.
with transport properties. A high ZT value of 0.39 was obtained at 1200 K. Our result is consistent with the past reported work on La atom doped SrTiO$_3$.

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References

1. G. J. Snyder, E. S. Toberer, World Sci., 101-110 (2011)
2. P. V. Arribi, P. García-Fernández, J. Junquera, V. Pardo. Phys Rev B, 94, 035124 (2016)
3. F. J DiSalvo. Sci., 285, 703-706 (1999)
4. I. T. Witting, T. C. Chasapis, F. Ricci, M. Peters, N. A. Heinz, G. Hautier, G. J. Snyder, Adv. Electron. Mater., 1800904 (2019)
5. A. A. Adewale, A. Chik, R. M. Zaki, F. C. Pa, C. K. Yeoh, N. H. Jamil, AIP Conference Proceedings, 2030, 020196 (2018)
6. V. K. Zaitsev, M. I. Fedorov, I. S. Eremin, E. A. Gurieva, D. M. Rowe, Thermoelectrics handbook: macro to nano, (2006)
7. H. Muta, K. Kurosaki and S. Yamanaka. J. Alloys Compd., 392, 306-309 (2005)
8. D. Srivastava, C. Norman, F. Azough, M. C. Schäfer, E. Guilmeau, R. Freer, J. Alloys Compd., 731, 723-730 (2018)
9. M. Ibáñez, D. Cadavid, R. Zamani, N. García-Castelló, V. Izquierdo-Roca, W. Li, A. Fairbrother, J. D. Prades, A. Shavel, J. Arbiol, A. Pérez-Rodriguez, Chem. Mater., 24, 562-570 (2012)
10. K. Park, J. S. Son, S. I. Woo, K. Shin, M. W. Oh, S. D. Park, T. Hyeon, J. Mater. Chem. A, 2, 4217-4224 (2014)
11. M. Saleemi, M. S. Toprak, S. Li, M. Johnsson, M. Muhammed, J. Mater. Chem., 22, 725-730 (2012)
12. T. Okuda, K. Nakanishi, S. Miyasaka, Y. Tokura. Phys Rev B, 63, 113104 (2001)
13. C. Chen, T. Zhang, R. Donelson, T. T. Tan, S. Li, J. Alloys and Compd., 629, 49-54 (2015)
14. Z. Lu, H. Zhang, W. Lei, D. C. Sinclair, I. M. Reaney, Chem. Mater., 28, 925-935 (2016)
15. A. A. Yaremchenko, S. Populoh, S. G. Patricio, J. Macfas, P. Thiel, D. P. Fagg, A. Weidenkaff, J. R. Frade, A. V. Kovalevsky, Chem. Mater., 27, 4995-5006 (2015)
16. J. Wang. Nano Energy, 35, 387-395 (2017)
17. A. V. Kovalevsky, M. H. Aguirre, S. Populoh, S. G. Patricio, N. M. Ferreira, S. M. Mikhailov, D. P. Fagg, A. Weidenkaff, J. R. Frade, J. Mater. Chem. A, 5, 3909-3922 (2017)
18. A. Tkach, J. Resende, K. V. Saravanan, M. E. Costa, P. Diaz-Chao, E. Guilmeau, O. Okhay, P. M. Vilarinho, ACS Sustain. Chem. Eng., 6, 15988-15994 (2018)
19. B. Zhang, J. Wang, T. Zou, S. Zhang, X. Yaer, N. Ding, C. Liu, L. Miao, Y. Li, Y. Wu, Y. J. Mater. Chem. C, 3, 11406-11411 (2015)
20. J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett., 77, 3865 (1996)
21. G. K. Madsen, D. J. Singh, Comput. Phys. Commun., 175, 67-71 (2006)
22. P. Blaha, K. Schwarz, G. K. Madsen, D. Kvasnicka, J. Luitz, *An augmented plane wave+ local orbitals program for calculating crystal properties*, (2001).
23. M. Cococcioni. *From Models to Materials Modeling and Simulation*, (2012).
24. H. J. Monkhorst, J. D. Pack, Phys. Rev. B, 13, 5188 (1976)
25. F. Birch, J. Appl. Phys., 9, 279-288 (1938)
26. A. Kokalj, J. Mol. Graph Model., 17, 176-179 (2000)
27. A. A. Mubarak, Int. J. Mod. Phys. B, 30, 1650141 (2016)
28. Z. Ali, I. Ahmad, A. H. Reshak, Physica B Condensed Matter, 410, 217-221 (2013)
29. P. Sikam, P. Moontragoon, C. Sararat, A. Karaphun, E. Swissitang, S. Pinitsoontorn, P. Thongbai, Appl. Surf. Sci., 446, 92-113 (2018)
30. S. Challagulla, R. Nagarjuna, S. Roy, R. Ganesan, Chemistry Select, 2, 4836-4842 (2017)
31. A. A. Adewale, A. Chik. IJNeaM, 12, 11-18 (2019)
32. W. J. Xie, Y. G. Yan, S. Zhu, M. Zhou, S. Populoh, K. Galazka, S. J. Poon, A. Weidenkaff, J. He, X. F. Tang, T. M. Tritt, Acta Mater., 61, 2087-2094 (2013)
33. X. Yan, G. Joshi, W. Liu, Y. Lan, H. Wang, S. Lee, J. W. Simonson, S. J. Poon, T. M. Tritt, G. Chen, Z. F. Ren, Nano Lett., 11, 556-560 (2010)
34. Y. Suzuki, H. Nakamura, Phys. Chem. Chem. Phys., 17, 29647-29654 (2015)
35. T. Wei, B. Xu, X. Ji, Eur. Phys. J. B, 92, 17 (2019)
36. M. J. Alrahamneh, A. A. Mousa, J. M. Khalifeh, Physica B Condens. Matter., 552, 227-235 (2019)
37. K. Kaur, R. Kumar, Chin. Phys. B, 25, 026402 (2016)
38. D. Liu, Y. Zhang, H. Kang, J. Li, Z. Chen, T. Wang, J. Eur. Ceram. Soc., 38, 807-811 (2018)
39. P. P. Shang, B. P., Zhang, Y. Liu, J. F. Li, H. M. Zhu, J. Electron. Mater., 40, 926-931 (2011)