Contents lists available at ScienceDirect

Surfaces and Interfaces

journal homepage: www.sciencedirect.com/journal/surfaces-and-interfaces

Underlying mechanism of surface (001) cubic $ATiO_3$ (A = Pb, Sn) in enhancing thermoelectric performance of thin-film application using density functional theory

N.N. Alam^{a,b}, N.A. Malik^{a,b}, M.H. Samat^b, N.H. Hussin^c, N.K. Jaafar^{a,b}, A. Radzwan^d, M. Z. Mohyedin^a, B.U. Haq^e, A.M.M. Ali^{a,b}, O.H. Hassan^{b,f}, M.Z.A. Yahya^g, M.F.M. Taib^{a,b,*}

^a Faculty of Applied Sciences, Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia

^b Ionic Materials and Devices (iMADE), Institute of Science, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

^c Faculty of Applied Sciences, Universiti Teknologi MARA (UiTM), 26400 Jengka, Pahang, Malaysia

^d Department of Physics, Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris, 35900 Tanjong Malim, Perak, Malaysia

^e Department of Physics, College of science, King Khalid University, Abha, Saudi Arabia

^f Faculty of Arts and Design, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

g Faculty of Defence Science & Technology, Universiti Pertahanan Nasional Malaysia, 57100 Kuala Lumpur, Malaysia

ARTICLE INFO

Keywords: Density functional theory Electronic properties Thermoelectric properties Surface (001)

ABSTRACT

 $PbTiO_3$ has emerged as a promising material for the thermoelectric application. In this study, we proposed to use density functional theory to investigate the underlying mechanism for improving the thermoelectric efficiency of ATiO_3. The thermoelectric parameters of the designed surface structures have been obtained by using the Boltzmann transport equation approximation. The properties of the structure, electronic, and thermoelectricity were measured and analyzed. The surface (001) modification through the AO termination layer has increased the electrical conductivity, thus increasing the power factor. On the other hand, increasing the Seebeck coefficient, which is aided by declining thermal conductivity, which is aided by low thermopower, improves the figure of merit. It is shown that the thermoelectric performance of surface (001) SnTiO_3 is higher as compared to PbTiO_3 making it interesting towards lead-free materials in thin-film application.

1. Introduction

Thermoelectric materials convert heat to electrical energy [1,2]. Some of the applications that have benefited from this conversion are temperature sensors, radiation detectors, solid-state thermoelectric cooling and spintronic [3,4]. Thermoelectric materials are gaining popularity due to their benefits, which include reliable conversion, scalability, and compactness as compared to other energy conversion technologies since there is no energy waste is generated during the activity which can solve the environmental problem [5]. Thermoelectric efficiency based on this energy conversion is identified by a dimensionless figure of merit $ZT = S^2 \sigma T/\kappa$, determined by Seebeck coefficient (S), electrical conductivity (σ), thermal conductivity (κ) and absolute temperature (T) [6]. According to the equation, a strong thermoelectric material has a higher thermopower and electrical conductivity, as well as a lower thermal conductivity. The highest ZT that lead (II) titanate,

PbTiO₃ (PTO) has ever attained is 1.7 which indicates highly promising thermoelectric material with the power factor of 0.002 $Wm^{-1}K^{-2}$ at 1000 K, accompanied by thermal conductivity, κ value of 1.15 $Wm^{-1}K^{-1}$ [7]. PTO has a relatively small unit cell that has high κ_L . However, it has been observed that anharmonicity, such as that seen in thermoelectric material like PbTe, can decrease κ_L despite small lattice constants [7,8]. Low thermal conductivity with favorable electronic transport values indicates the great promise of PTO and tin (II) titanate, SnTiO₃ (SnTO) as a thermoelectric material [9]. The electrical conductivity can be maintained through alloying or increasing the complexity of the unit cell while having low thermal conductivity [10,11]. Despite this promise, only a limited number of experimental results are available at room-temperature and high-temperature behavior of κ_L in ferroelectrics including PTO [12,13]. Computational prediction of κ_L could illuminate some of these points. With this in mind, a semiclassical analysis of κ_L and the electronic transport parameters of PTO are reported in this work.

* Corresponding author: Universiti Teknologi MARA, Malaysia. *E-mail address:* mfariz@uitm.edu.my (M.F.M. Taib).

https://doi.org/10.1016/j.surfin.2021.101524

Received 16 August 2021; Received in revised form 23 September 2021; Accepted 7 October 2021 Available online 17 October 2021 2468-0230/© 2021 Elsevier B.V. All rights reserved.







The calculations are based on Boltzmann transport equations (BTE), BoltzTrap which rely on ab initio results as the input. This study predicts very low κ_L and high thermoelectric potential for PTO. As a result, it is predicted that the power factor and ZT of thermoelectric characteristics may be fine-tuned and improved.

 $ATiO_3$ (A = Pb, Sn) is a perovskite structure and known to exhibit considerable power factor to establish high-performance thermoelectric materials [14]. Perovskite-type oxides which are well known to have phase transition also have been investigated due to their cheap cost and excellent thermal resilience against high temperature sintering [15,16]. The investigation of the enhancement mechanism of PTO and SnTO thermoelectric is done through the graph analysis of electrical conductivity, thermal conductivity, Seebeck coefficient, power factor and ZT [17]. Theoretical report by Noor et al. exhibits the consistent pattern in which values of PF increase with the rise of temperature for both bulk PTO and SnTO up to 4.45 \times 10^{11} $Wm^{-1}k^{-2}s^{-1}$ and 4.8 \times 10^{11} $Wm^{-1}k^{-2}s^{-1}$ s at 800 K, respectively [9]. Subsequently, the power factor and ZT contribute in various ways to reach their maximum value. Both, however, are aided by n-type doping at their optimal levels to achieve a maximum value at 300 K. [18,19]. Cubic bulk PTO and SnTO have higher power factor (PF) as they have higher electrical conductivity compared to the surface structure (001). The thermal performance of bulk PTO and SnTO can be enhanced by focusing on achieving higher PF while in surface structure, it can be achieved by increasing the ZT since they have higher thermopower. In realizing this contribution, it will provide fundamental parameters in enhancing thermoelectric performance. Hence, investigating the surface structure of ATiO₃ could enormously influence the macroscopic of unconstrained polarization and the piezoelectric reaction [20]. On the other hand, for nanoscale ferroelectrics, which have higher surface-to-volume proportions than bulk materials, the surface impact becomes significant. Thus, by focusing on the (001) cubic surface since it has the lowest surface energy compared to other surfaces [21]. Interestingly, there is less work on ABO3 pervoskites regarding PTO (001) surface considering their huge potential in the nanoscale application. Furthermore, there is no work at all for surface SnTO reported yet considering its importance to reduce the consumption of lead (II) in thin-film application [22].

According to a theoretical report by Eglitis et al. [21] the absence of surface electrons in AO-terminated (001) surfaces for SrTiO₃, BaTiO₃ and PTO and the presence of special lone pair hybridization of Pb 6 s in PTO is significant for any further treatment of electrical conductivity of surface defects on perovskite surface. Meyer et al. [23] found that surface (001) cubic and tetragonal PTO is enhanced at the PbO terminated surface and suppressed at TiO2 terminated surface. Padilla and Vanderbilt [24] investigated the (001) surface of SrTiO₃ and discovered that the surface layer of the Sr-terminated surface has no large ferromagnetic deviation, whereas the ferroelectric instability of the Ti-terminated surface has become so unbalanced that it can be easily destroyed by thermal disruptions. In this work, we employed density functional theory (DFT) to investigates the structural, electronic and thermoelectric properties of ATiO_{3.} The investigation was focusing on the AO termination (001) surfaces of PTO and SnTO using CASTEP computer code and BoltzTrap. Using surface (001) of ATiO3 increases the thermoelectric properties [25]. Therefore, a semiclassical investigation of κ_L and the electronic properties of PTO and SnTO are accounted for in this work as no hypothetical works are investigating its surface (001) thermoelectric properties so far.

2. Computational methods

The cubic structure of $ATiO_3$ (A = Pb, Sn) with the space group Pm3m is used [26,27]. The structural parameter was compared with the previous experimental report by Wang [28]. The structural and electronic properties were calculated within Materials Studio in CASTEP computer code. Ultrasoft pseudopotential was used for optimization to ensure the accuracy of calculation with regard to fully convergent

all-electron DFT calculations. Generalize gradient approximation-Perdew Burke Ernzerhof (GGA-PBE) is chosen as functional exchange-correlation [29,30]. The cut-off energy was 350 eV and the k-point was $4 \times 4 \times 4$ Monkhorst-pack [31,32]. All atom forces were reduced to less than 0.03 eV Å⁻¹, the highest ionic displacement was reduced to 0.001, and the overall stress tensor was reduced to 0.05 GPa [33,34].

The cubic structure is cleaved to become (001) surface structure which consists of three layers with a vacuum of 12 is applied [31]. The vacuum region is enlarged to three times of the theoretical lattice constant thick. This result showed that the vacuum region is enough for these systems. Since the surface structure is (001), the vacuum is applied on z-axis to prevent repetition of cell at the z-axis. The surface structure is optimized by using GGA-PBE functional with cut-off energy of 350 eV and a k-point of $4 \times 4 \times 4$ Monkhorst-Pack [35,36]. Table 2 shows the surface relaxation of cubic (001) ATiO₃ (A = Pb, Sn). The quantity s compute the outer displacement of the primary surface oxygen towards the first layer metal atoms, Δd_{12} is the difference in primary interlayer distance, as estimated from the surface to the subsurface metal z-coordinate, and Δd_{23} is measured from the second layer to third layer [34, 37]. The positive values indicate the relaxations outward the vacuum region while the negative values indicate the relaxations inward the vacuum region. All the magnitudes of atom displacements respect to ideal positions are given as fraction of the cubic lattice constant. The calculated surface energy of (001) which is shown in Table 2 for both AO and TiO₂ terminated surface is almost equivalent. The surface energy for PTO is comparable with other theoretical works [21]. It is reported that the surface energy of 001<011<111 [38]. In order to calculate the surface relaxation and surface (001) energy are given, respectively as [38]

$$\delta_{i,\ i+1} = \frac{d_{i,\ i+1} - a_0/2}{a_0} \times 100\% \tag{1}$$

$$E_{surf} = \frac{1}{4} \left(E_{slab}^{AO} + E_{slab}^{TiO_2} - 7E_{bulk} \right)$$
⁽²⁾

The structures of these surfaces were optimized using the fullpotential linearized-augmented plane-wave (FP-LAPW) [39,40]. The thermoelectric properties have been obtained by using semi-classical BolzTrap in WIEN2K computer code. The properties can be computed based on the calculated band structure on the rigid band approach [41]. The contribution of Seebeck coefficient (S), electrical conductivity (σ), thermal conductivity (κ), power factor and ZT were determined. The equation for both electron and hole carrier as the electrical conductivity, Seebeck coefficient and thermal conductivity for zero point charge across a material are given, respectively, as [8]

$$\sigma = \frac{e^2 m_d^{3/2}}{\pi^2} \int_0^\infty \frac{-\partial f^0}{\partial E} \tau \overline{\nu}^2 k^{*2} dk^*$$
(3)

$$S = \frac{-m_d^3}{T\sigma\pi^2} \int_0^\infty \frac{-\partial f^0}{\partial E} \tau \bar{\nu}^2 (E - E_F) k^{*2} dk^*$$
(4)

$$\kappa_0 = \frac{m_d^3}{T\pi^2} \int_0^\infty \frac{-\partial f^0}{\partial E} \tau \overline{\nu}^2 (E - E_F)^2 k^{*2} dk^*$$
(5)

where f^0 is the Fermi-Dirac distribution, e is the charge of electron, k^* are the rescaled wave vectors with respect to the valley minimum in the spherical coordinate system, E_F is the Fermi energy level, m_d is the DOS effective mass, τ is the relaxation time and $\overline{\nu}$ is the average group velocity.

Fig. 1 shows the (001) surface structure of cubic $ATiO_3$. The GGA-PBE function is used to perform geometrical optimization, and the corresponding experimental and theoretical values are reported in Table 1.



Fig. 1. Unit cell of cubic surface (001) structure of $ATiO_3$ (A = Pb, Sn) with AO terminated on the left and TiO_2 terminated on the right. The gray, red and silver colors represent the Pb/Sn, O and Ti atoms, respectively.

The estimated lattice parameter is compatible with the findings of other experimental and theoretical studies with a slight difference of 0.08-0.99%.

3. Results and discussion

3.1. Electronic band structure

Electronic properties which are band structure and DOS were determined after structural optimization. The GGA-PBE function was used to calculate the band structure. Fig. 2 shows the band structures of the PTO and relaxes surface structures of terminated PbO and TiO₂. The

calculated energy bands of the bulk PTO are distinctively different as compared for the two types (terminated PbO and TiO₂) surface structures. Both are uniformly transferred, resulting in the metal atom in the central layer of 1 s core level energy aligning with the bulk system. PbO terminated surface in PTO has a band gap of 1.572 eV gap that is almost equivalent to the bulk structure which is 1.691 eV compared to TiO₂ terminated surface which is 1.366 eV. As a result, the band gap of the PbO terminated surface shrinks. In comparison to the bulk system, the band states of O p around 0 eV on the type-I surface tend to expand upward, particularly at the A stage. The surface state appears at the A stage, in contrast with the bulk band structure. A similar shift is noticeable on the type-II surface, especially at the D stage.

Similar band structures observed for bulk SnTO and the relaxed surface structures of SnO and TiO₂ terminated are shown in Fig. 3. A distinctively different of the bulk SnTO was observed with surface SnO and TiO₂ terminated. The calculated energy bands for the two types of surface structures are uniformly transferred, as they are for PTO. The type-I surface of SnTO has an indirect band gap of 1.159 eV, whereas the type-II surface has a band gap of 1.196 eV. As a result, the band gap of the type-I surface SnTO is nearly identical to the bulk device. The surfaces state appears to lie beneath the conduction band as the top of the valence band is slightly lower than the bulk.

Table 2

Calculated surface rumpling, s, interlayer displacements, Δd_{ij} (in percent of bulk lattice constant) and surface energy (eV) for AO and TiO₂ terminated (001) surfaces of PTO and SnTO.

Compounds		s	Δd_{12}	Δd_{23}	Surface energy (eV)
	AO termination				
	(type-I)				
PTO (001)	This work	3.80	-6.82	3.89	0.85
	Previous results [23]	4.00	-6.80	3.40	-
	Previous results [46]	3.51	-6.89	3.07	0.83
	Previous results [47]	3.90	-6.75	3.76	0.97
SnTO (001)	This work	3.78	-6.76	3.82	0.71
	TiO ₂ termination				
	(type-II)				
PTO (001)	This work	3.10	-7.70	5.21	0.75
	Previous results [23]	3.20	-7.90	5.50	-
	Previous results [46]	3.12	-8.13	5.32	0.74
	Previous results [47]	3.06	-7.93	5.45	-
SnTO (001)	This work	2.96	-7.10	5.10	0.68

Table 1

Calculated lattice parameters, (Å), volume, (Å³) and respective percentage differences (%) of PTO and SnTO using CASTEP with available theoretical and experimental research.

Method	Basis set	a (Å)	Percentage difference (%)	V (Å ³)	Percentage difference (%)
This work	РТО				
LDA-CAPZ	Plane wave	3.892	+1.71 [43]	58.9683	+5.04 [43]
			+1.97 [44]		+5.76 [44]
GGA-PBE	Plane wave	3.973	-0.33 [43]	62.7176	-0.99 [43]
			-0.08 [44]		-0.23 [44]
GGA-PBEsol	Plane wave	3.929	+0.78 [43]	60.6730	+2.29 [43]
			+1.04 [44]		+3.03 [44]
B3PW [21]	Gaussian-type	3.936		60.9811	
LDA [42]	LAPW	3.973		62.7152	
B3PW [38]	Gaussian-type	3.963		62.2458	
Expt. [43]		3.950		62.5708	
Neutron-diffraction					
Expt. [44]		3.969		62.5235	
Synchrotron-radiation					
This work	SnTO				
LDA-CAPZ	Plane wave	3.849		57.0611	
GGA-PBE	Plane wave	3.941		61.2004	
GGA-PBEsol	Plane wave	3.907		59.6346	
LDA-CAPZ [45]	Plane wave	3.850		57.0667	
GGA-PBE [46]	Plane wave	3.966		62.3818	



Fig. 2. The band structure of PTO (a) projected bulk band structure, (b) Pb O terminated surface (type-I) and (c) TiO₂ terminated surface (type-II), the solid lines represent the band structure in the Brillouin Zone. The top of valence bands is set to be zero.



Fig. 3. The band structure of SnTO (a) projected bulk band structure, (b) Sn O terminated surface (type-I) and (c) TiO₂ terminated surface (type-II), the solid lines represent the band structure in the Brillouin Zone. The top of valence bands is set to be zero.

3.2. Electronic density of states (DOS)

The DOS for the two types of the surface structures were evaluated to analyze the structure of the band structure. Figs. 4 and 5 illustrate the DOS for bulk and partial DOS dissected into layers for the PTO and SnTO termination, accordingly. The top of O p at the terminating surface has shifted to increased energy indicates the band gap of type-I surface has reduced compared to the DOS of O atoms in the central layer as shown in Figs. 4 and 5. Furthermore, there is a minor difference in partial DOS of Pb and Sn p in the various layers as the interaction between Pb/Sn p and O p in the surfaces structures is similar to the bulk structure as reported previously [48]. The hybridization between the first layer Pb 6 s and second layer O 2p is stronger than that between the third layer Pb 6 s and central layer O 2p for type-I termination as shown in Fig. 4(b). The hybridization between the central layer Pb 6 s and third layer O 2p is shown for type-II termination in Fig. 4(c). In Fig. 5(b) and 5(c), for the type-I termination, there is an enhancement of the Sn-O bond covalency in the second layer between the Sn and O atoms since the hybridization between the first layer Sn 5 s and second layer O 2p is considerably

increased. For the type-II termination, the hybridization between the second layer Sn and first layer O is somewhat increased contrasted to that in bulk or the SnTO central layer. However, the behavior of the band gap for PTO and SnTO type-II termination is distinctive compared to $SrTiO_3$ and $BaTiO_3$. It is shown that Ba does not contribute to valence band or conduction band, despite the fact that it provides electrons to balance the system charge [49,50]. According to Meyer et al. [23], the suppression of certain O 2p and Ti 3d hybridization has caused the band gap to result in an upward interference of the top valence band states, while in PTO and SnTO the reduction of band gap between conduction and valence bands are inhibited due to the strong covalent Pb-O and Sn-O interaction.

3.3. Thermoelectric transport parameters

Thermoelectric transport properties specifically focusing on the type-I terminated surface since it is considerably enhanced at AO termination and suppressed at TiO_2 termination. The fundamental band structure, on the other hand, cannot be changed. In semiconducting materials, the



Fig. 4. (a) DOS of cubic bulk of PTO, (b) DOS of each layer for PbO terminated surface (type-I) (c) DOS of each layer for TiO_2 terminated surface (type-II) of PTO.

electrical conductivity (σ) provides free carriers for the conduction operation. The Fermi level is found within the band gap of semiconductors. As temperature rises, energy transfer will occur between the charge carriers from the valence band to the conduction band. In an n-type semiconductor, charge carriers are electrons, and in a p-type semiconductor, charge carriers are holes. Fig. 6 and Fig. 8 show the σ/τ and SnTO from 300 to 800 K, demonstrating that the σ/τ nearly remains stable as the temperature rises. The calculated values of σ/τ for PTO and SnTO at room temperature are 1.7×10^{17} S/ms and 4.09×10^{18} S/ms, respectively. Since the small band distance increases the probability of carriers moving in the conduction band, the graph of the σ/τ curve for SnTO is higher than that of PTO.

The Seebeck coefficient (S) which is also called thermopower, is calculated by dividing the voltage shift across a material by the temperature difference $S = \Delta V / \Delta T$ [51,52]. The formula to calculate the potential temperature gradient at zero current density also can be



Fig. 5. (a) DOS of cubic bulk of SnTO, (b) DOS of each layer for SnO terminated surface (type-I) (c) DOS of each layer for TiO_2 terminated surface (type-II) of SnTO.

written using the relation $J = -\sigma \nabla V - \sigma S \nabla T$ The current density is represented by J, the potential gradient by ∇V , and the temperature gradient by ∇T . The Seebeck coefficient for zero current density also can be reduced to the differential form of $\nabla V = S \nabla T$. The temperature gradient of potential increases even more dramatically for PTO than for SnTO in our studied compounds as temperature rises. Furthermore, the SnTO value is higher at room temperature than PTO, while at a higher temperature, the S for PTO exceeds SnTO due to the cancelation of carrier current.

The thermal conductivity (κ/τ) of the material is another significant parameter that provides information on heat conduction across crystal lattices in terms of electron and phonon energy. Materials with high thermal conduction values are typically used for heat sink applications, whereas materials with low thermal conduction values are suitable for thermal insulation [53]. The phononic contribution is derived from mechanical elastic waves produced by lattice vibration as temperature rises, while the electronic contribution is derived from the contribution



Fig. 6. Seebeck coefficient (S), electrical conductivity (σ/τ) and power factor (PF) of cubic (001) PTO against Fermi energy. The peak value of PF is represented by dotted lines of each temperature from 300 K to 800 K.

of the free carrier. Since the phononic contribution is very small in semiconductors, thus it is ignored to simplify the calculation. Fourier's law which can be described as $q = -k\nabla T$ is the heat efflux with temperature is used to explain κ/τ . In Figs. 7 and Fig. $9\kappa/\tau$ against temperature for PTO and SnTO has been plotted. Since SnTO electric bandgap is smaller than PTO, the slope of the SnTO curve is higher. The smaller the band distance, the easier it is for electrons to move from the valence band to the conduction band and transfer heat.

The Wiedemann-Fraz theorem describes the ratio of thermal to electrical conductivity, $LT=\kappa/\sigma.$ For the best thermoelectric materials, the value should be having the lowest value of LT. The PF can describe the thermoelectric efficiency of the device. The value of S in our study semiconductor compounds is increasingly proving the hole as the dominant carrier. Furthermore, the values of PF for both PTO and SnTO increase with increasing temperature, reaching 3.11×10^{11} W/mK 2 s and 3.40×10^{11} W/mK 2 s at 800 K, respectively. Since the effect of S is greater, the slope of PF for SnTO is higher than that of PTO.

The increase in Seebeck coefficient and thermal conductivity also influence the peak of figure of merit (ZT). In order to estimate thermal efficiency to obtain the optimum thermal performance, ZT is also used.



Fig. 7. Seebeck coefficient (S), thermal conductivity (κ/τ) and figure of merit (ZT) of cubic (001) PTO against Fermi energy. The peak value of PF is represented by dotted lines of each temperature from 300 K to 800 K.



Fig. 8. Seebeck coefficient (S), electrical conductivity (σ/τ) and power factor (PF) of cubic (001) SnTO against Fermi energy. The peak value of PF is represented by dotted lines of each temperature from 300 K to 800 K.



Fig. 9. Seebeck coefficient (S), thermal conductivity (κ/τ) and figure of merit (ZT) of cubic (001) SnTO against Fermi energy. The peak value of PF is represented by dotted lines of each temperature from 300 K to 800 K.

Via the relationship $ZT = S^2 \sigma T/\kappa$, the ZT increases with increasing σ/τ and S^2 while decreasing with κ/τ . Lower thermal conductivity will give higher ZT values. Thermal conductivity is contributed by the electronic thermal conductivity and lattice thermal conductivity ($\kappa = \kappa_e + \kappa_L$) [54–56]. The calculated ZT values are still underestimated since in the transport theory, the lattice thermal conductivity is not included. Therefore, the ZT values are higher. The results of the calculation are shown in Figs. 7 and 9. It is shown at 300 K the ZT peak is contributed by a higher value Seebeck coefficient which is $-2040 \mu V/K$ and lower thermal conductivity. However, it can be seen highest ZT peak occurred

Table 3

Thermoelectric properties parameters for electrical conductivity (σ/τ), power factor (PF) and figure of merit (ZT) of cubic surface (001) PTO and SnTO at room temperature (300 K) and 800 K.

	Electrical conductivity, σ/τ	Power factor, PF (W/	Figure of merit, ZT
	(S/ms)at 300 K:	mK ² s)at 800 K:	at 300 K:
PTO SnTO	$\begin{array}{c} 1.7\times 10^{17} \\ 4.09\times 10^{18} \end{array}$	$\begin{array}{l} 3.11 \times 10^{11} \\ 3.40 \times 10^{11} \end{array}$	0.93 0.97

at 400 K to 500 K. PTO and SnTO have ZT values of 0.93 and 0.97 at 300 K, respectively. Table 3 below summarizes all thermoelectric properties that have been discussed. It shows that thermoelectric properties of SnTO are higher as compared to PTO.

4. Conclusion

In this study, the theoretical calculation shows that the thermoelectric performance of ATiO₃ can be enhanced through surface modification such as surface (001). The DFT calculation of structural, band structure and DOS is enhanced at AO terminated surface while suppressed at TiO₂ terminated surface (001). AO termination also increases the electronic properties and overall thermoelectric performance compared to bulk PTO and SnTO. Bulk PTO and SnTO have higher PF while surface (001) PTO and SnTO have higher ZT. Higher electrical conductivity is contributed by larger DOS and smaller electronic band gap. PF is enhanced as the electrical conductivity increases with the reducing Seebeck coefficient while ZT can be enhanced by increasing the Seebeck coefficient and reducing the electrical conductivity with thermal conductivity. We found that PTO and SnTO are significantly enhanced thermoelectric performance through the surface (001) termination. Furthermore, SnTO has higher PF and ZT which indicates a higher overall thermoelectric performance than that of PTO. These interesting strategies show SnTO as a promising nontoxic material to develop high-performance thermoelectric material to reduce the consumption of lead for future thin-film applications.

CRediT authorship contribution statement

N.N. Alam: Conceptualization, Formal analysis, Investigation, Writing – original draft, Methodology, Data curation, Visualization. N. A. Malik: Formal analysis, Methodology, Software, Data curation. M.H. Samat: Supervision, Validation, Writing – review & editing. N.H. Hussin: Supervision, Validation, Writing – review & editing. N.K. Jaafar: Supervision, Validation, Writing – review & editing. A. Radzwan: Methodology, Software, Data curation. M.Z. Mohyedin: Methodology, Software, Writing – review & editing. B.U. Haq: Supervision, Validation, Writing – review & editing. B.U. Haq: Supervision, Validation, Writing – review & editing, Funding acquisition. A.M.M. Ali: Supervision, Validation, Writing – review & editing. M.Z.A. Yahya: Software, Supervision, Validation, Writing – review & editing. M.F.M. Taib: Software, Validation, Resources, Supervision, Writing – review & editing, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by the Ministry of Higher Education (MOHE) Malaysia under UiTM Excellent Fund (600-RMC/KEPU 5/3 (008/2021)). Most appreciate to Universiti Teknologi MARA (UiTM) and Ionics, Materials and Devices (iMADE) Research Laboratory for the facilities provided. The author (Bakhtiar Ul Haq) extends his appreciation to the Deanship of Scientific Research at King Khalid University for funding his work through Research Groups Program under Grant No. R. G.P. 2/126/42.

References

 Y. Zhang, Y.J. Heo, M. Park, S.J. Park, Recent advances in organic thermoelectric materials: principle mechanisms and emerging carbon-based green energy materials, Polymers (Basel) 11 (2019), https://doi.org/10.3390/polym11010167.

- [2] M.A. Zoui, S. Bentouba, J.G. Stocholm, M. Bourouis, Research progress and application of thermoelectric generator, Energies 13 (14) (2020), https://doi.org/ 10.3390/en13143606.
- [3] T. Wu, P. Gao, Development of perovskite-type materials for thermoelectric application, Materials (Basel) 11 (2018) 999, https://doi.org/10.3390/ ma11060999.
- [4] Y. Zhang, Y.J. Heo, M. Park, S.J. Park, Recent advances in organic thermoelectric materials: principle mechanisms and emerging carbon-based green energy materials, Polymers (Basel) 11 (2019), https://doi.org/10.3390/polym11010167.
- [5] X. Tang, X. Wang, R. Cattley, F. Gu, A.D. Ball, Energy harvesting technologies for achieving self-powered wireless sensor networks in machine condition monitoring: a review, Sensors 18 (2018) 4113, https://doi.org/10.3390/s18124113.
- [6] P. Torres, J.A. Seijas-Bellido, C. Escorihuela-Sayalero, J. Íniguez, R. Rurali, Theoretical investigation of lattice thermal conductivity and electrophononic effects in SrTiO3, Phys. Rev. Mater. 3 (2019) 1–6, https://doi.org/10.1103/ PhysRevMaterials.3.044404.
- [7] A. Roy, Estimates of the thermal conductivity and the thermoelectric properties of PbTiO3 from first principles, Phys. Rev. B. 93 (2016) 3–7, https://doi.org/ 10.1103/PhysRevB.93.100101.
- [8] R. D'Souza, J. Cao, J.D. Querales-Flores, S. Fahy, I. Savić, Electron-phonon scattering and thermoelectric transport in p -type PbTe from first principles, Phys. Rev. B. 102 (2020) 1–14, https://doi.org/10.1103/PhysRevB.102.115204.
- [9] N.A. Noor, Q. Mahmood, M. Rashid, B. Ul Haq, A. Laref, S.A. Ahmad, Ab-initio study of thermodynamic stability, thermoelectric and optical properties of perovskites ATiO3 (A=Pb, Sn), J. Solid State Chem. 263 (2018) 115–122, https:// doi.org/10.1016/j.jssc.2018.04.017.
- [10] F.F. Jaldurgam, Z. Ahmad, F. Touati, Low-toxic, earth-abundant nanostructured materials for thermoelectric applications, Nanomaterials 11 (2021) 895, https:// doi.org/10.3390/nano11040895.
- [11] M.Z. Mohyedin, M.F.M. Taib, A. Radzwan, M. Mustaffa, A. Shaari, O.H. Hassan, B. U. Haq, M.Z.A. Yahya, Enhanced mechanism of thermoelectric performance of Bi 2 Se 3 using density functional theory, Mater. Renew. Sustain. Energy. 9 (2020) 1–9, https://doi.org/10.1007/s40243-020-00176-4.
- [12] H.H. Somaily, Tuning structural and physical properties via A-site doping in perovskite-type transition metal oxides, (2018). https://commons.lib.niu.edu/h andle/10843/21646.
- [13] Y. Fu, D.J. Singh, Thermal conductivity of perovskite KTaO 3 and PbTiO 3 from first principles (2018).
- [14] H. Fang, Y. Wang, S. Shang, Z.K. Liu, Nature of ferroelectric-paraelectric phase transition and origin of negative thermal expansion in PbTi O3, Phys. Rev. B -Condens. Matter Mater. Phys. 91 (2015) 1–6, https://doi.org/10.1103/ PhysRevB.91.024104.
- [15] S. Goumri-Said, S. Azam, S.A. Khan, M.B. Kanoun, Density functional theory within spin-orbit coupling and hubbard correction for investigation of optoelectronic properties of the orthorhombic perovskite LaPdO3, Comput. Condens. Matter. 21 (2019) e00396, https://doi.org/10.1016/j.cocom.2019.e00396.
- [16] M. Ghazanfar, S. Azam, M. Nasir, S. Goumri-Said, H. Alrobei, Insight into electronic and optical properties of Eu b2 -doped CaTiO 3 from GGAbU calculations, J. Solid State Chem. 293 (2020), https://doi.org/10.1016/j.jssc.2020.121796.
- [17] K.H. Park, M. Mohamed, Z. Aksamija, U. Ravaioli, Phonon scattering due to van der Waals forces in the lattice thermal conductivity of Bi2Te3 thin films, J. Appl. Phys. 117 (2015), 015103, https://doi.org/10.1063/1.4905294.
- [18] G. Rahman, A. Rahman, Thermoelectric properties of n and p -type Cubic and Tetragonal X TiO 3 (X = Ba,Pb): a Density Functional Theory Study, Phys. B Condens. Matter. (2017) 526, https://doi.org/10.1016/j.physb.2017.07.044.
- [19] G. Xing, J. Sun, K.P. Ong, X. Fan, W. Zheng, D.J. Singh, Perspective: n -type oxide thermoelectrics via visual search strategies, APL Mater. 4 (2016) 1–7, https://doi. org/10.1063/1.4941711.
- [20] S. Hosseini, T. Movlarooy, A. Kompany, First-principle calculations of the cohesive energy and the electronic properties of PbTiO 3, Physica B-Condens. Matter - Phys. B 391 (2007) 316–321, https://doi.org/10.1016/j.physb.2006.10.013.
- [21] R. Eglitis, Ab initio calculations of CaZrO 3, BaZrO 3, PbTiO 3 and SrTiO 3 (001), (011) and (111) surfaces as well as their (001) interfaces, Integr. Ferroelectr. 196 (2019) 7–15, https://doi.org/10.1080/10584587.2019.1591976.
- [22] R. Eglitis, Ab initio hybrid DFT calculations of BaTiO3, PbTiO3, SrZrO3 and PbZrO3 (111) surfaces, Appl. Surf. Sci. 358 (2015) 556–562, https://doi.org/ 10.1016/j.apsusc.2015.08.010.
- [23] B. Meyer, J. Padilla, D. Vanderbilt, Theory of PbTiO 3, BaTiO 3, and SrTiO 3 Surfaces. 0849(1999), 1–13. https://doi.org/10.1039/A903029H.
- [24] J. Padilla, D. Vanderbilt, Ab initio study of BaTiO 3 surfaces, Phys. Rev. B 56 (1997) 1625, https://doi.org/10.1103/PhysRevB.56.1625.
- [25] L. Peng, Z. Liu, Enhancing thermoelectric properties by using a surface polarization effect based on PEDOT:PSS thin films, J. Mater. Chem. C. 7 (2019) 6120–6128, https://doi.org/10.1039/C8TC06616G.
- [26] S. Kuma, M.M. Woldemariam, Structural, electronic, lattice dynamic, and elastic properties of SnTiO3 and PbTiO3 using density functional theory, Adv. Condens. Matter Phys (2019), https://doi.org/10.1155/2019/3176148.
- [27] M.F.M. Taib, M.K. Yaakob, F.W. Badrudin, M.S.A. Rasiman, T.I.T. Kudin, O. H. Hassan, M.Z.A. Yahya, First-Principles Comparative Study of the Electronic and Optical Properties of Tetragonal (P4mm) ATiO3 (A = Pb,Sn,Ge), Integr. Ferroelectr 155 (2014) 23–32, https://doi.org/10.1080/10584587.2014.905105.
- [28] P.Yuan L.Wang, F. Wang, E.J. Liang, Q. Sun, Z.X. Guo, Y. Jia, First-principles study of tetragonal PbTiO3: phonon and thermal expansion, Mater. Res. Bull. 49 (2014) 509–513, https://doi.org/10.1016/j.materresbull.2013.08.075.

- [29] R. Cuevas-Saavedra, V.N. Staroverov, Exact expressions for the Kohn–Sham exchange-correlation potential in terms of wave-function-based quantities, Mol. Phys. 114 (2016) 1050–1058, https://doi.org/10.1080/00268976.2015.1131861.
- [30] N.N. Alam, N.A. Malik, M.H. Samat, M.Z. Mohyedin, N.H. Hussin, A.M.M. Ali, O. H. Hassan, M.Z.A. Yahya, M.F.M. Taib, First principles study on structural and electronic properties of cubic (Pm3m) and tetragonal (P4mm) ATiO3 (A=Pb, Sn), Sci. Res. J. 17 (2020) 149, https://doi.org/10.24191/srj.v17i2.9918.
- [31] T. Nishimatsu, M. Iwamoto, Y. Kawazoe, U.V. Waghmare, First-principles accurate total energy surfaces for polar structural distortions of BaTiO3, PbTiO3, and SrTiO3: consequences for structural transition temperatures, Phys. Rev. B -Condens. Matter Mater. Phys. 82 (2010) 1–9, https://doi.org/10.1103/ PhysRevB.82.134106.
- [32] M.F.M. Taib, M.K. Yaakob, F.W. Badrudin, T.I.T. Kudin, O.H. Hassan, M.Z. A. Yahya, First-principles calculation of the structural, elastic, electronic and lattice dynamics of GeTiO3, Ferroelectrics 452 (2013) 122–128, https://doi.org/10.1080/ 00150193.2013.841525.
- [33] J. Sifuna, P. García-Fernández, G.S. Manyali, G. Amolo, J. Junquera, Firstprinciples study of two-dimensional electron and hole gases at the head-to-head and tail-to-tail 180° domain walls in PbTiO3 ferroelectric thin films, Phys. Rev. B. 101 (2020) 1–7, https://doi.org/10.1103/PHYSREVB.101.174114.
- [34] M.F.M. Taib, M.K. Yaakob, A. Chandra, A.K. Arof, M.Z.A. Yahya, Effect of pressure on structural, electronic and elastic properties of cubic (Pm3m) SnTiO3 using firstprinciples calculation, Adv. Mater. Res. (2012), https://doi.org/10.4028/www. scientific.net/AMR.501.342.
- [35] M.F.M. Taib, M.K. Yaakob, O.H. Hassan, A. Chandra, A.K. Arof, M.Z.A. Yahya, First principles calculation on structural and lattice dynamic of SnTiO3 and SnZrO3, Ceram. Int. 39 (2013) S297–S300, https://doi.org/10.1016/j. ceramint.2012.10.081.
- [36] M.F.M. Taib, M.K. Yaakob, O.H. Hassan, M.Z.A. Yahya, Structural, electronic, and lattice dynamics of PbTiO3, SnTiO3, and SnZrO3: a comparative first-principles study, Integr. Ferroelectr 142 (2013) 119–127, https://doi.org/10.1080/ 10584587,2013,780528.
- [37] K. Garrity, A. Kakekhani, A. Kolpak, S. Ismail-Beigi, Ferroelectric surface chemistry: first-principles study of the PbTiO 3 surface, Phys. Rev. B - Condens. Matter Mater. Phys. 88 (2013) 1–11, https://doi.org/10.1103/ PhysRevB.88.045401.
- [38] R.I. Eglitis, D. Vanderbilt, Ab initio calculations of BaTi O3 and PbTi O3 (001) and (011) surface structures, Phys. Rev. B - Condens. Matter Mater. Phys. 76 (2007) 1–10, https://doi.org/10.1103/PhysRevB.76.155439.
- [39] P. Blaha, K. Schwarz, G.K. Madsen, D. Kvasnicka, and J. Luitz, Computer Code WIEN2K, Vienna University of Technology (2001).
- [40] M. Zhong, W. Zeng, F.S. Liu, B. Tang, Q.J. Liu, First-principles study of the atomic structures, electronic properties, and surface stability of BaTiO3 (001) and (011) surfaces, Surf. Interface Anal. 51 (2019) 1021–1032, https://doi.org/10.1002/ sia.6688.
- [41] G.K. Madsen, D.J. Singh, BoltzTraP. A code for calculating band-structure dependent quantities, Comput. Phys. Commun. 175 (2006) 67–71, https://doi.org/ 10.1016/j.cpc.2006.03.007.
- [42] T. Scheidemantel, C. Ambrosch-Draxl, T. Thonhauser, J.V. Badding, J.O. Sofo, Transport coefficients from first-principles calculations, Phys. Rev. B 68 (2003), 125210, https://doi.org/10.1103/PhysRevB.68.125210.

- Surfaces and Interfaces 27 (2021) 101524
- [43] Y. Kuroiwa, S. Aoyagi, A. Sawada, J. Harada, E. Nishibori, M. Takata, M. Sakata, Evidence for Pb-O covalency in tetragonal PbTiO3, Phys. Rev. Lett. 87 (2001), 217601, https://doi.org/10.1103/PhysRevLett.87.217601 b.
- [44] R.J. Nelmes, W.F. Kuhs, The crystal structure of tetragonal PbTiO3 at room temperature and at 700 K, Solid State Commun. 54 (1985) 721–723, https://doi. org/10.1016/0038-1098(85)90595-2.
- [45] Y. Wang, M. Arai, T. Sasaki, C. Wang, W.L. Zhong, First-principles study on the (001) surface of cubic PbZrO3 and PbTiO3, Surf. Sci. 585 (2005) 75–84, https:// doi.org/10.1016/j.susc.2005.04.015.
- [46] X. Chen, A. Zhang, J. Wang, Q. Luo, G. Tang, J. Zhang, D. Bai, Band alignments and polarization properties in ZnO (112⁻⁰)/PbTiO3 (001) heterostructures, Vacuum 166 (2019) 264–269, https://doi.org/10.1016/j.vacuum.2019.05.013.
- [47] G. Pilania, R. Ramprasad, Adsorption of atomic oxygen on cubic PbTiO3 and LaMnO3 (001) surfaces: a density functional theory study, Surf. Sci. 604 (2010) 1889–1893, https://doi.org/10.1016/j.susc.2010.07.021.
- [48] N.N. Alam, N.A. Malik, N.H. Hussin, A.M.M. Ali, O.H. Hassan, M.Z.A. Yahya, M.F. M. Taib, First-principles study on electronic properties, phase stability and strain properties of cubic (Pm3m) and tetragonal (P4mm) ATiO3 (A=Pb, Sn), 13 (2020) 281–288.
- [49] A. Alshoaibi, M.B. Kanoun, B. Ul Haq, S. AlFaify, S. Goumri-Said, Insights into the impact of yttrium doping at the Ba and Ti sites of BaTiO3 on the electronic structures and optical properties: a first-principles study, ACS Omega 5 (2020) 15502–15509, https://doi.org/10.1021/acsomega.0c01638.
- [50] A. Alshoaibi, M.B. Kanoun, B. Ul Haq, S. AlFaify, S. Goumri-Said, Ytterbium doping effects into the Ba and Ti sites of perovskite barium titanate: electronic structures and optical properties, Results Phys. 18 (2020), 103257, https://doi.org/10.1016/ j.rinp.2020.103257.
- [51] M.S. Dresselhaus, Y.M. Lin, S.B. Cronin, M.R. Black, O. Rabin, G. Dresselhaus, Investigation of low-dimensional thermoelectrics, in: Proc. Nonlithogr. Lithogr. Methods Nanofabrication Symp., Technomic Publishing Co, Lancaster, Pa, USA, 2001. https://doi.org/10.1134/1.1130849.
- [52] T. Takeuchi, Conditions of electronic structure to obtain large dimensionless figure of merit for developing practical thermoelectric materials, Mater. Trans. (2009), 908170873, https://doi.org/10.2320/matertrans.M2009143.
- [53] H. Fang, Y. Wang, S. Shang, Z.K. Liu, Nature of ferroelectric-paraelectric phase transition and origin of negative thermal expansion in PbTi O3, Phys. Rev. B -Condens. Matter Mater. Phys. 91 (2015) 1–6, https://doi.org/10.1103/ PhysRevB.91.024104.
- [54] S. Azam, S.A. Khan, S. Goumri-Said, Optoelectronic and Thermoelectric Properties of Bi2OX 2 (X = S, Se, Te) for Solar Cells and Thermoelectric Devices, J. Electron. Mater. 47 (2018) 2513–2518, https://doi.org/10.1007/s11664-018-6092-1.
- [55] S. Azam, S. Goumri-Said, S.A. Khan, H. Ozisik, E. Deligoz, M.B. Kanoun, W. Khan, Electronic structure and related optical, thermoelectric and dynamical properties of Lilianite-type Pb7Bi4Se13: ab-initio and Boltzmann transport theory, Materialia 10 (2020), 100658, https://doi.org/10.1016/j.mtla.2020.100658.
- [56] Y. Benazouzi, H. Rozale, M.A. Boukli Hacene, M. Khethir, A. Chahed, D. Lucache, Electronic and thermoelectric properties in Li-based Half-Heusler compounds: a first principle study, Ann. West Univ. Timisoara - Phys. 61 (2019) 44–55, https:// doi.org/10.2478/awutp-2019-0004.