Insights into Structural, Electronic and Thermoelectric Properties of ZnTMN$_2$ (TM= Zr and Hf): A First-Principles Study

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We employ first-principles calculations combined with semi classical Boltzmann transport theory to investigate the structural, electronic, and thermoelectric properties of ZnTMN$_2$ (TM= Zr and Hf). The negative value of formation energy confirms the stability of these compounds. We used Tran Blaha modified Becke Johnson approximation to calculate electronic properties. ZnZrN$_2$ and ZnHfN$_2$ are having indirect bands of magnitude 2.77 eV and 3.31 eV, respectively. The positive value of the Seebeck Coefficient at all studied temperatures confirms its p-type nature. The thermal conductivity slightly decreases with a rise in temperature in ZnHfN$_2$ as compared to ZnZrN$_2$. The observed value of the figure of merit is 0.80 and 0.81 at 500 K and 600 K for ZnZrN$_2$ and ZnHfN$_2$, respectively. The high figure of merit of Hf and Zr-based nitrides make them a potential material for thermoelectric energy harvesting applications.

Keywords: DFT; Becke johnson approximation; Electronic properties; Seebeck coefficient; Thermoelectric energy harvesting

1 Introduction

The unprecedented demand of energy led to over-consumption of natural resources resulting in devastating natural calamities in recent times. The green energy harvesting techniques are emerging as an alternate to conventional energy resources to sage guard the environment. Thermoelectric (TE) materials have been considered as one of the potential candidates for the green energy harvesting given its peculiar merits over the other conventional energy resources *i.e.*, wind energy and solar energy[1,2]. The efficiency these materials characterized by a dimensionless quantity[1], figure of merit which is represented as ZT = $S^2\sigma T/\kappa_e + \kappa_l$. Here, S, σ, κ_e, and κ_l denote the Seebeck coefficient, electrical conductivity, electronic thermal conductivity, and lattice thermal conductivity, respectively. To find effective TE material the extensive research has been carried out on various materials, including oxide[3], Zintl[4], and nitrides[5]. Among the semiconductors, nitrides are considered as the promising candidate owing to their high radiation resistance, high chemical stability and thermal stability which are advantageous for TE applications[6,7]. We examined the structural, electronic and transport properties using first-principles calculation in combination with Boltzmann transport theory of ZnTMN$_2$ (Tm = Zr, Hf) as a potential TE material.

2 Computational Methods

The ab-initio calculations were performed using Density Functional Theory (DFT) based wien2k code[8]. The generalized gradient approximation (GGA) scheme of Perdew-Burke-Ernzerhof (PBE) was used to optimize the lattice parameters of the studied systems[9]. As GGA scheme underestimate the band gap, so for realistic prediction of various properties, we were employed Tran-Blaha modified Becke-Johnson (TB-mBJ) potential[10] which incorporates exchange and correlation energy that uses semi local quantities. The strict energy convergence of 0.0001 Ry was used. A Γ-centred k-mesh of 15×15×11 was employed to sample the Brillouin zone. The transport properties were obtained by solving semi classical Boltzmann transport equation under constant relaxation time approximation which are implemented in the BoltzTraP code[11]. A denser k-mesh of 45×45×33 was used for transport calculations.

3 Results and Discussion

3.1 Structural and Electronic Properties

The ZnTMN$_2$ (Tm = Zr, Hf) exist in hexagonal structure with space group *P3m1*[12]. The crystal structure exists in TM^{4+}, Zn^{2+}, and N^{3-} environment.

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In which the TM^{4+} is coupled to six N^{3-} atoms to produce TMN$_6$ octahedra that share corners with six ZnN$_4$ tetrahedra, edges with six TMN$_6$ octahedra, and edges with three ZnN$_4$ tetrahedra. There are three short bonds and three long bonds of bond length 2.13 Å and 2.33 Å, respectively in Zr-N, this bond length reduces in the case of Hf-N to 2.11 Å and 2.30 Å, respectively. The optimised lattice parameters are listed in Table 1.

The model crystal structure and optimized lattice parameters are presented in Fig. 1. The optimised structure is further used to evaluate the electronic and transport properties.

To further examine the properties of the purposed compound it is vital to check the thermodynamical stability. The stability analysis is done by the formation energy which is given by the formula[4]:

$$E_f = \{E_{total} - n(E_{Zn} + E_{TM} + E_N)\}/M \qquad ... (1)$$

where, M is the total number of elements in the unit cell, E$_{total}$ is the total energy of the cell, E$_{Zn}$, E$_N$, and E$_{TM}$ is the energy of individual Zn, N, TM (Zr and Hf) atom, respectively.

The negative formation energy confirms the thermal stability of the proposed materials. A large negative value of formation energy shows the more stable behaviour of ZnHfN$_2$.

The electronic band structure of ZnTMN$_2$ (Tm = Zr, Hf) is obtained using TB-mBJ as shown in Fig. 2. It is observed that ZnZrN$_2$ and ZnHfN$_2$ have indirect band gap for of 2.77 eV and 3.31 eV, respectively along M-Γ points.

Table 1 — The lattice parameters (in Å) and formation energy of ZnTMN$_2$ (Tm = Zr, Hf).

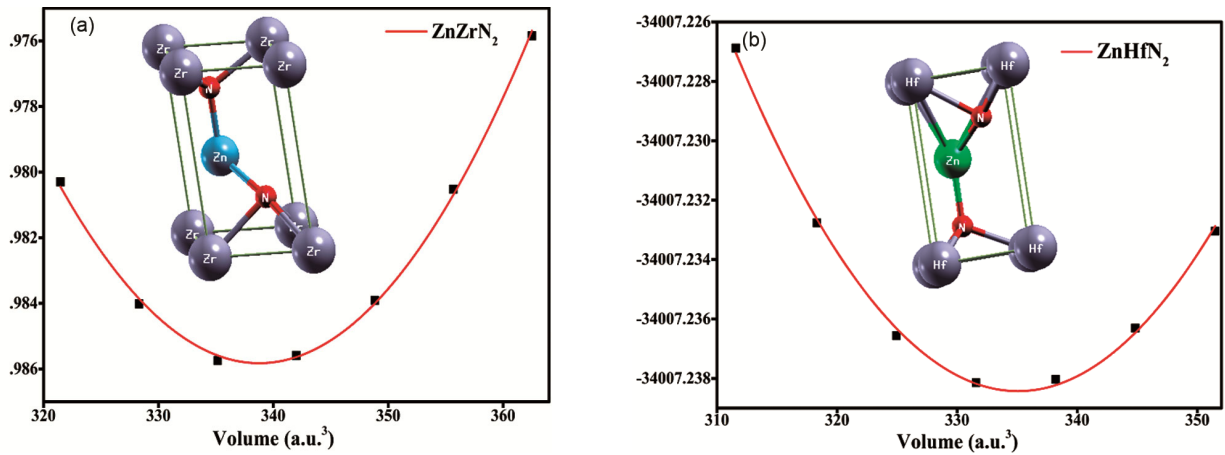|	a	b	c	Formation energy (eV)
ZnZrN$_2$	3.26	3.26	5.25	-1.044
ZnHfN$_2$	3.25	3.25	5.27	-1.171

Fig. 1 — The energy vs volume curve and crystal structure (inset) of ZnTMN$_2$ (Tm = Zr, Hf).
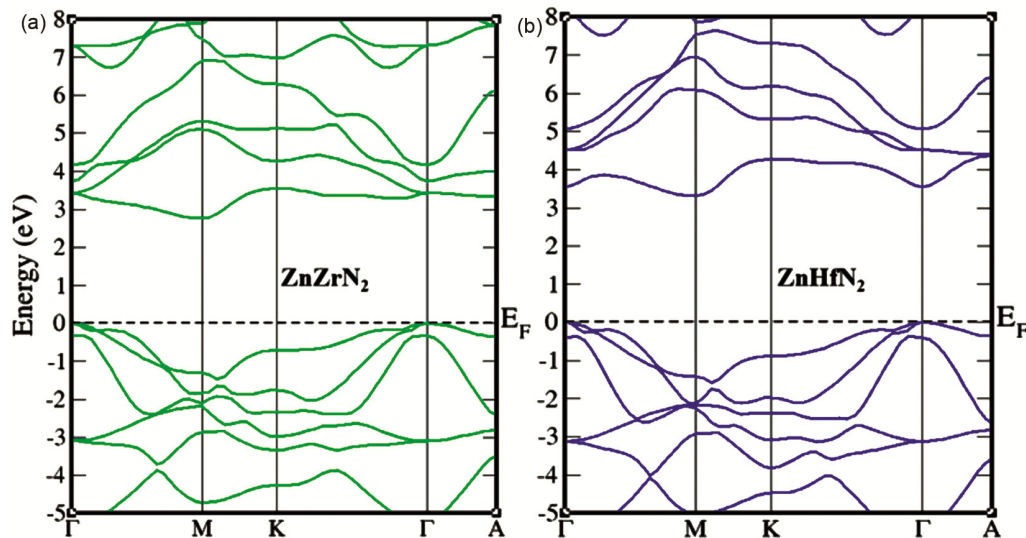
Fig. 2 — The electronic band structure of ZnTMN$_2$ (Tm = Zr, Hf). The Fermi level set to 0 eV.
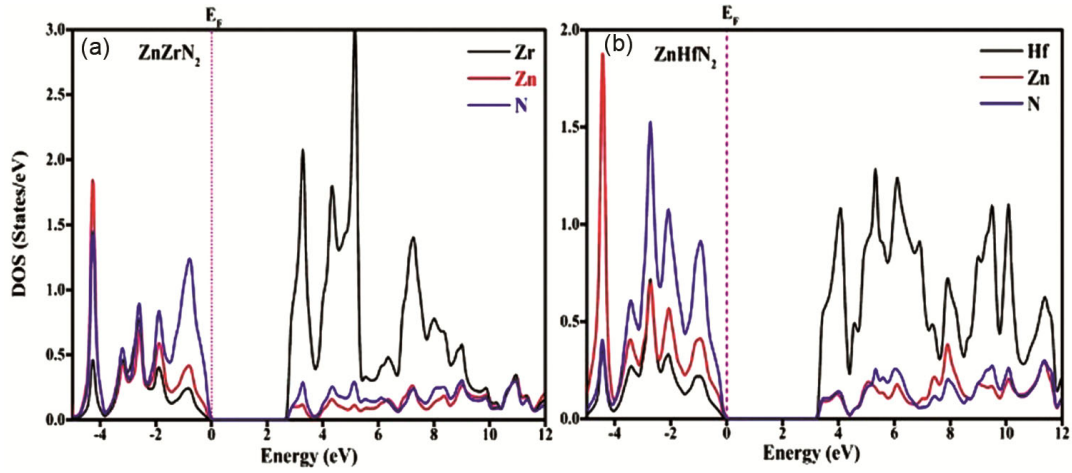
Fig. 3(a,b) — The density of states of ZnTMN$_2$ (Tm = Zr, Hf).

The density of states (DOS), Fig. 3, shows that in the valence band (VB) the N-atomic states dominant and in the deep VB the Zn-atomic states show major contribution over others. Whilst, in the conduction band (CB) Zr-atomic states more prominent over others. The magnitude of hybridization is decreases as we move from ZnZrN$_2$ to ZnHfN$_2$ this might be due to complex bonding nature of the compounds.

We have analyzed the electronic charge density contour plot along (010) plane, which shows that the mix covalent and ionic bonding in both compounds. The extent of covalent bonding is more in case of ZnZrN$_2$ (Fig. 4). The large hybridization in Zr-Zn-N atomic states in DOS is also reflected in the charge density plot.

3.2 Transport Properties

The accurate band gap estimation is important to investigate the TE behaviour of these materials for realistic comparison with future experiments. We have obtained the precise band gap using TB-mBJ potential. The TE parameters are calculated through the solution of the BTE under rigid band approximation. The S, σ, κ are the main parameters which effect TE performance. We have investigated the effect of temperature on these parameters. The variation of S with the temperature describes the ability of material to generate electric potential. The value of S rises with increase in temperature and attain the maximum value 276.59 μVK^{-1} at 900 K and 274.57 μVK^{-1} at 950 K for ZnZrN$_2$ and ZnHfN$_2$, respectively (Fig. 5 (a)).This slight variation in the values of S might be high DOS of Zr near the fermi
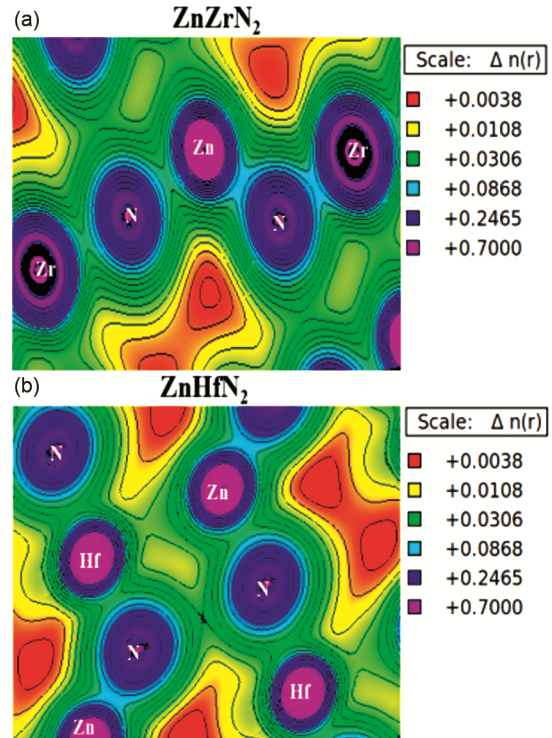

Fig. 4 — The electronic charge density of ZnTMN$_2$ (Tm = Zr, Hf).

level. The positive value of S represents the p-type behaviour of both materials.

The behaviour of σ/τ and κ/τ with temperature are shown the Fig. 5(b,c). At room temperature the value of σ/τ is 0.11x10^{19} Ω^{-1}m^{-1}s^{-1}, whereas at 1200 K it increases to 1.32x10^{19} Ω^{-1}m^{-1}s^{-1} and 1.26x10^{19} Ω^{-1}m^{-1}s^{-1} for ZnZrN$_2$ and ZnHfN$_2$, respectively. The calculated value of κ/τ at room temperature is 0.029x10^{15} WmK^{-1}s^{-1} whereas at 1200 K the values are
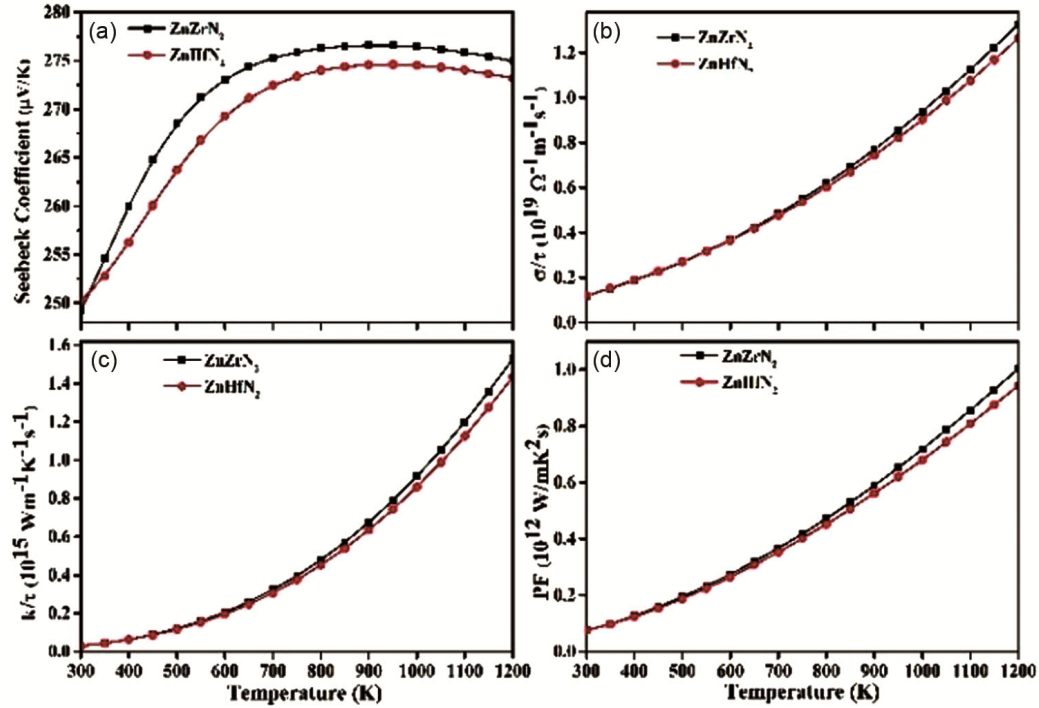
Fig. 5 — The variation of (a) Seebeck coefficient (b) electrical conductivity (c) electronic thermal conductivity (d) power factor ofZnTMN$_2$ (Tm = Zr, Hf) at different temperatures.
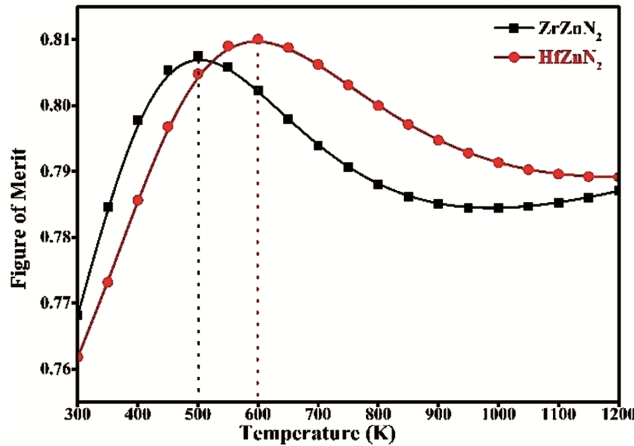

Fig. 6 — Figure of merit of ZnTMN$_2$ (Tm = Zr, Hf).

1.529x10^{15} WmK^{-1}s^{-1} and 1.43x10^{15} WmK^{-1}s^{-1} for ZnZrN$_2$ and ZnHfN$_2$, respectively.

The variation in the PF with temperature is shown in Fig. 5 (d). The observed value at room temperature is 0.074x10^{12} Wm^{-1}K^{2}s^{-1}, whereas at 1200 K the obtained values are 1x10^{12} Wm^{-1}K^{2}s^{-1} and 0.94x10^{12} Wm^{-1}K^{2}s^{-1}.

The variation of ZT with temperature is shown in Fig. 6. At room temperature the ZT for both materials is ~0.76. As temperature increases ZT starts increases up to 500 K with magnitude 0.80 and 600 K with magnitude 0.81 for ZnZrN$_2$ and ZnHfN$_2$, respectively. The slight increase in ZT for ZnHfN$_2$ is due to its low electronic thermal conductivity.

4 Conclusion

We have examined the structural, electronic and TE properties of ZnTMN$_2$ (Tm = Zr, Hf). The negative value of formation energy has confirmed the thermodynamical stability of purposed compounds. The indirect band of magnitude 2.77 eV and 3.31 eV have calculated for ZnZrN$_2$ and ZnHfN$_2$, respectively. The magnitude of charge sharing has been confirmed by DOS and electronic charge density contour plot. The observed value of the figure of merit are 0.80 and 0.81 at 500 K and 600 K for ZnZrN$_2$ and ZnHfN$_2$, respectively. The high figure of merit of Hf and Zr-based nitrides make them a promising candidate for thermoelectric green energy harvesting applications.

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