Algerian Journal of Research and Technology
https://doi.org/10.58681/ajrt.21050106
A.J.R.T Volume 5 (N°1) (2021) 52 - 60

Theoretical Study of Electronic and Thermoelectric Properties of Sodium Doped 4H-GaN Polytype

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Received. March 28, 2020. Accepted. December 23, 2020. Published. March 22, 2021.

DOI: https://doi.org/10.58681/ajrt.21050106

Abstract. In this work, the electronic and thermoelectric properties of co-doped 4H-GaN polytype with (Na-Na) are studied using Quantum Espresso code based on norm-Conserving pseudo potential. The exchange-correlation energy was treated under the Generalized Gradient Approximation (GGA).It is interesting to note that the calculated band structure of sin up state shows a direct band gap (Γ- Γ) semiconductor with a small direct band gap (0.023 eV). While spin down state shows a metallic behavior. It indicates that 4H-GaN:Na-Na is found to be half-metallic ferromagnetic with total magnetic moment of 4.00µB. The transport properties of this material are studied using the semi-classical Boltzmann theory implanted in the BoltzTraP code. The electrical conductivity, the beck coefficient, the electronic thermal conductivity, the electronic power factor and the merit factor, as a function of temperature at fixed chemical potential were obtained for this polytype. The ZT values found for this co-doped polytype at 400K temperature are 1.01 and 0.03 respectively for spin up and down states. We therefore expect these alloys to be potential candidates for the thermoelectric applications.

Keywords. DFT, Half-metallic ferromagnetic, Co-doped 4H-GaN polytype, BoltzTrap.

INTRODUCTION

The two most known thermoelectric effects are the beck effect (Seebeck, 1822) (generation of a voltage from a temperature gradient) and the Peltier effect (generation of a temperature gradient from an electric current) (Peltier, 1834). The beck coefficient (S), the electrical conductivity (σ/τ) where τ represents relaxation time, the thermal conductivity ($S^2\sigma/\tau$), the thermoelectric power factor (κ_e/τ) and the figure of merit (ZT) are the most important thermoelectric properties. The first three parameters are independent; they are used to classify thermoelectric materials (Rowe , 1995). Indeed, a good thermoelectric material has a high beck coefficient, low thermal conductivity and high electrical conductivity (Altenkirch,

1909). A material with a unit ZT equal to or greater than unity is considered the best candidate for thermoelectric devices. The ZT values of the best commercial thermoelectric material such as the Bi2Te3 alloy is about 0.9 at room temperature (Rowe, 1995). The majority of existing thermoelectric devices are now based on materials Bi2Te3 and Sb2Te3 (for ambient temperatures), PbSnTe (for intermediate temperatures) and PbTe (for high temperatures) (Rowe, 1995; Kulbachinskii et al., 2012; Orihashi et al., 2000; Niino et al., 1997). These materials are rare, toxic and unstable at elevated temperatures. In recent years, intense efforts have been devoted to discovering new thermoelectric materials. GaN and its alloys are promising candidates for high temperature thermoelectric materials due to their high beck coefficient and high thermal and mechanical stability. There has been very little experimental work done on the thermoelectric properties of GaN and its alloys. To the best of our knowledge, no theoretical analysis of the thermoelectric properties of GaN material has ever been reported. The measured value of the beck coefficient, electrical conductivity and the thermal conductivity were –50 μV/K, $0.523\times10^{+4}$ $(\Omega.m)^{-1}$ and 2.6 W/mK for undoped GaN at 300K, respectively (Yamamoto and Yamaguchi, 2004). It was found that the thermoelectric figure of merit for GaN at 300K is about 0.0017 (Yamamoto and Yamaguchi, 2004; Weili and Balandin; 2005). An intense research activity of new thermoelectric materials has attracted considerable scientific interest. Remarkable efforts have been made to develop new thermoelectric materials from the doping of GaN wurtzite polytypes (pH-GaN, p = 2, 4 and 6) (Bechstedt and Belabbes, 2013). The power factors of pH-GaN show a very weak dependence on the polytype. Their figure of merit strongly increases with increasing temperature (Zheng et al., 2015). Calculation of the thermoelectric properties of Gd doped GaN (GaN: Gd) and Mg doped GaN (GaN:Mg), showed that the bek coefficient, the electrical conductivity are respectively -209 μV /K and 17.48 $(\Omega.cm)^{-1}$ for GaN:Gd and 710 at 900 μV/K for GaN:Mg (Hurwit et al., 2011; Kucukgok et al., 2015). The most currently adopted strategies to achieve this goal are based primarily on the doping of polytypes of GaN with transition metals (Dietl et a., 2000; Mahadevan and Zunger , 2004). A recent study (Torrichi et al., 2018), based on the doping of the 4H-GaN polytype by the pair of atoms (Na,Na), revealed that this material presented a magnetic moment of $4.00\mu_B$. The study of state density has shown that this polytype is half-metallic ferromagnetic. It should be mentioned that no experimental or theoretical study has been reported in the literature on the thermoelectric properties of this polytype. In this work, we have study the electronic band structure and the thermoelectric properties of the 4H-GaN:Na-Na material in its most stable structure. Beck coefficient, electrical conductivity, thermal conductivity, thermoelectric power factor and merit factor were calculated using BoltzTraP code, hoping that this work will serve as a support for a practical study of thermoelectricity.

COMPUTATIONAL METHOD

The electronic structure calculations were performed using density functional theory (DFT) with the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) (Perdew et al., 1996) using plane wave pseudo potential method as implemented in Quantum Espresso package (Giannozzi et al., 2009). We employed the Troullier–Martins norm-conserving pseudo potentials (Troullier and Martins, 1991). A cutoff energy for plane waves of 80Ry is chosen,an energy cutoff of 400Ry was included for the charge density, and a Gaussian smearing of 0.02Ry is applied. Integration on the Brillouin zone is computed within a 8×8×6k-point Monkhorst-Pack mesh (Monkhorst and Pack, 1976).Calculations proceeded self-consistently until the total energy converged to within 0.1meV/cell. The BoltzTraP (Madsen and Singh, 2006) code was also used to calculate the thermoelectric properties such the electrical conductivity (σ/τ), beck coefficient (S), electronic thermal conductivity ($\kappa e/\tau$), power factor ($S^2\sigma/\tau$)and figure of merits (ZT).

RESULTS AND DISCUSSIONS

Structural properties

The undoped 4H-GaN structure adopted in our work contains four gallium (Ga) atoms and four nitrogen (N) atoms (Figure 1). Doping consists in replacing two gallium atoms by two Na atoms, which gives us six possibilities of arrangements, noted (ci,cj).In order to determine the most stable structure, we calculated their cohesion energies. The Murnaghan equation of state is applied to determine the equilibrium energy (Murnaghan, 1944). The results of the structural parameters, the cohesion energies and the total magnetic moments are shown in Table 1. Our results show that configuration structure (c2,c4) is the most stable. They are in perfect agreement with another theoretical work based on DFT (Torrichi et al., 2018). Finally, note that the total magnetic moment obtained for the most stable configuration is ($4\mu_B$) characterizing the half-metallic nature of 4H-Gan:Na-Na.The total magnetic moment is in good agreement with a previous calculation (Torrichi et al., 2018). It should be mentioned that no experience has been reported in the literature.

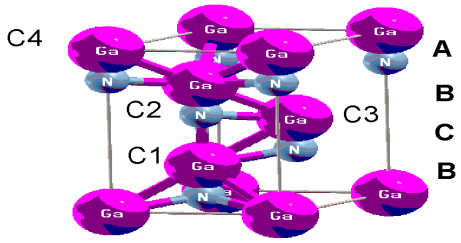

Fig. 1. Crystal structure of 4H-GaN polytype.

Table 1. The structural parameter (a, c/a), the cohesive energy (E_{coh}) and the total magnetic moment (M_{tot}) of 4H-GaN:Na-Na polytype.

Sites (i,j)	Works	a (Å)	c/a	Ecoh (eV)	M (μB)
(c1,c2)	Present PBE-NC	3.439	1.783	-28.726	3.94
	Other DFT *	3.440	1.648	−4.064	4.00
(c1,c3)	Present PBE-NC	3.442	1.804	-27.868	3.93
	Other DFT *	3.423	1.689	−3.988	3.98
(c1,c4)	Present PBE-NC	3.336	1.953	-28.194	3.99
	Other DFT *	3.377	1.746	−4.171	4.00
(c2,c3)	Present PBE-NC	3.494	1.686	-28.762	3.99
	Other DFT *	3.495	1.579	−4.010	3.99
(c2,c4)	Present PBE-NC	3.598	1.670	-30.609	4.00
	Other DFT *	3.454	1.616	−4.186	4.00
(c3,c4)	Present PBE-NC	3.437	1.791	-29.423	4.00
	Other DFT *	3.438	1.645	−4.108	4.00

*(Torrichi et al., 2018)

Electronic properties

To know the nature of our material, we studied its band structure; they are shown in figure 2(a-b). The band structures are plotted along the high symmetry M → Γ→ A principal symmetry direction of the Brillouin zone of the hexagonal lattice in the majority spin bands (spin-up) and minority spin bands (spin-down). Figure 2(b) shows that the spin-polarized band structure exhibits metallic behavior for the minority state channel, while the majority spin channel exhibits a Fermi deviation (Figure 2). It is observed that valence band maximum and conduction band minimum are located at Γ point, confirming the direct nature of band gap in this co-doped polytype. Direct band gap at Γ symmetry point having value of 1.83eV for spin-up configuration has been noted. This result show that (Na,Na)-co-doped 4H-GaN material is half metallic ferromagnetic. The energy band structures are in good agreement with the energy band gaps presented in previous work of DOS calculations (Torrichi et al., 2018).

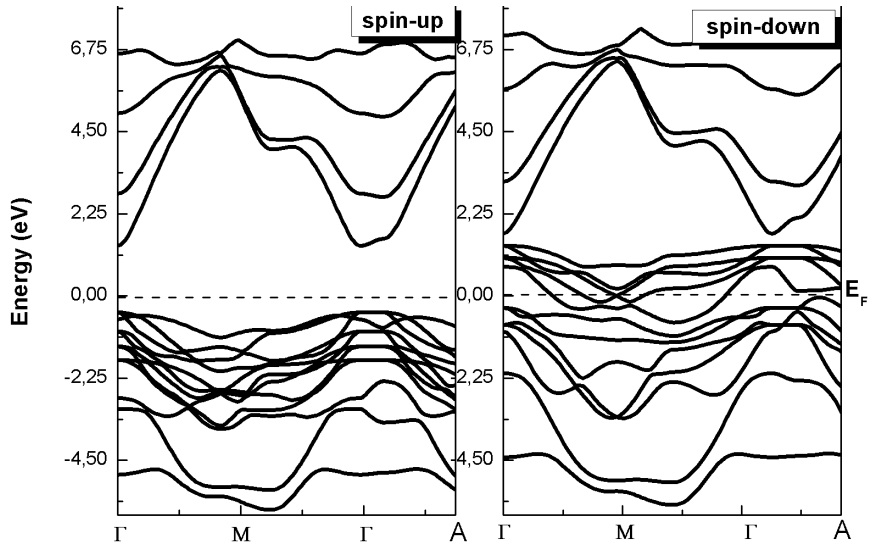

Fig. 2. Band structures of 4H-GaN:Na-Na polytype for the WZ phases**.**

Thermoelectric properties

For calculation of thermoelectric properties of 4H-GaN:Na-Na polytype, we have made use of semi-classical Boltzmann theory as employed in BoltzTraP code. In order to have potential thermoelectric properties in a material, it needs to have large value of electrical conductivity, large value of beck coefficient and very low electronic thermal conductivity. In the present paper, we have reported the thermoelectric parameters in the temperature range of 50K to 800K. We have computed thermoelectric parameters like electrical conductivity (σ/τ), where τ, represents relaxation time, beck coefficient (S), electronic thermal conductivity ($\kappa e/\tau$) and power factor ($S^2\sigma/\tau$) and graph of merit (ZT) in range of 50K to 800K. We have plotted all thermoelectric properties at a fixed chemical potential ($\mu = E_F$=4.860912eV) where E_F is Fermi energy.

Figure 3(a-b) shows the variation of electronic thermal conductivity with temperature for 4H-GaN:Na-Na polytypic material in both spin up and down states. The value of $\kappa e/\tau$ increases slightly with temperature from 50K to 500Kin spin up state. Beyond 500K, we notice a strong variation of the dependent electronic thermal conductivity. $\kappa e/\tau$ increases from $0.0011\times10^{+14}$ W/mks at 500K to $0.0646\times10^{+14}$ W/mks at 800K. In spin down states $\kappa e/\tau$ increases sharply with temperature. $\kappa e/\tau$ increases from $0.8611\times10^{+14}$ W/mks at 50K to $16.7736\times10^{+14}$ W/mks

at 800K. The decreasing trend of κe/τ presents the metallic nature of the compound in spin down states.

We have shown in figure 4(a-b) the variation of electrical conductivity as a function of temperatures for 4H-GaN:Na-Na polytype material in both spin up and down states. They indicate that at 300K, the values of this electrical conductivity are respectively $2.1472\times10^{+11}$ $(\Omega.m.s)^{-1}$ and $7.1387\times10^{+19}(\Omega.m.s)^{-1}$ for spin up and down states. In spin up states, the electrical conductivity values remain constant in the temperature range between 50K and 500K, from this value the electrical conductivity increases rapidly up to 800K. In spin down states, electrical conductivity increases sharply with temperature. The decreasing trend of σ/τ presents the metallic nature of the compound in spin down states. The slow increasing nature of σ/τ in spin up states presents the semi-conducting nature of the compound. Materials with high values of electrical conductivity are required for thermoelectric applications.

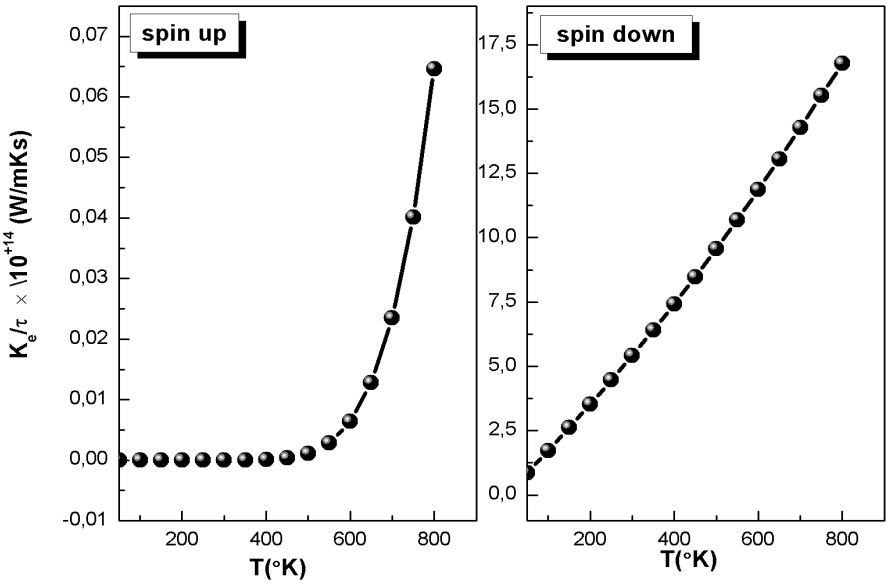

Fig. 3. The calculated thermal conductivity of 4H-GaN:Na-Na polytype versus temperature (a) Spin up state, (b) Spin down state.

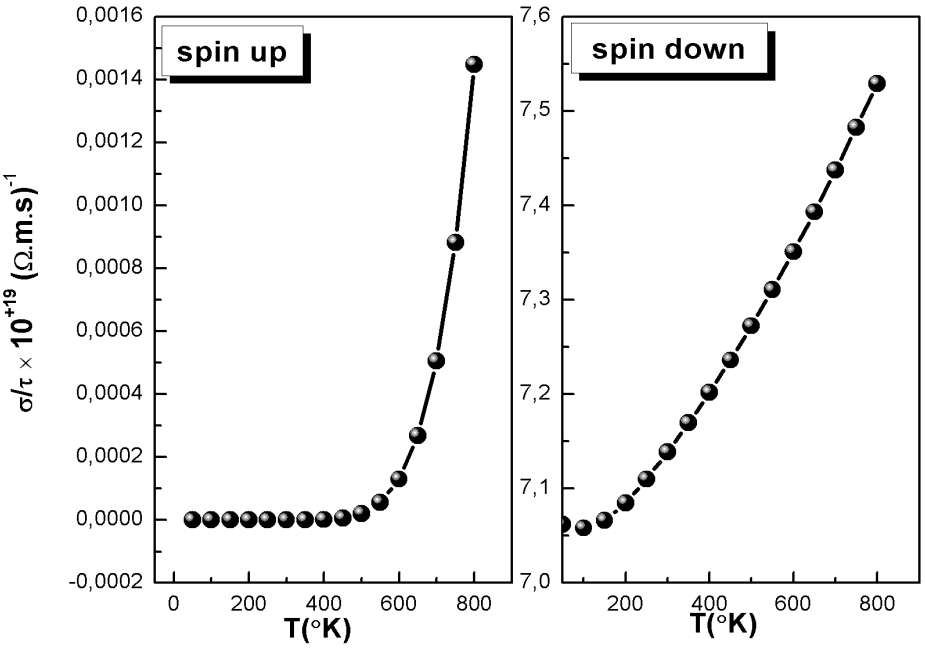

Fig. 4. The calculated electrical conductivity of 4H-GaN:Na-Na polytype versus temperature (a) Spin up state, (b) Spin down state.

The thermoelectric materials are classified according to their beck (S) coefficients; the good ones are those with a large S coefficient. Figure5 (a-b) shows the variation curves of the beck coefficient as a function of the temperature for 4H-GaN:Na-Na polytype. It is clearly observed from the plot that the calculated values of the (S) is positive in the entire temperature range for spin up states and negative for spin down states. This is the clear indication that charge carriers in spin up states are positive while in spin down states these are negative. In spin up state, beck coefficient decrease from 2180 μV/K (200K) to721 μV/K (800K). In spin down state, this value increase from -3.71 μV/K (at 50 K) to -30.03 μV/K (at 400K). The power factor ($S^2\sigma/\tau$) is a very important quantity to study the transport properties in a solid. It determines its ability to produce electrical energy for a given temperature. Figure 6(a-b) presents power factor for 4H-GaN:Na-Na compound against temperature, in both spin up and down states, at 300K temperature. The figure 6(b) shows that, in spin down state, $S^2\sigma/\tau$ increases rapidly from $97.33\times10^{+11}$W/mK^{2}s at 50K to 6496.74W/mK^{2}s at 400K, then this quantity decrease until 3458.8349 W/mK^{2}s at 800K. In spin up state, the value of $S^2\sigma/\tau$ increases slightly with temperature. The value of $S^2\sigma/\tau$ in spin up state is found to increase from $0.05\times10^{+11}$W/mk^{2}s at 300K to $755.17\times10^{+11}$W/mk^{2}s at 800K. A material with a unit ZT equal to or greater than unity is considered the best candidate for thermoelectric devices.

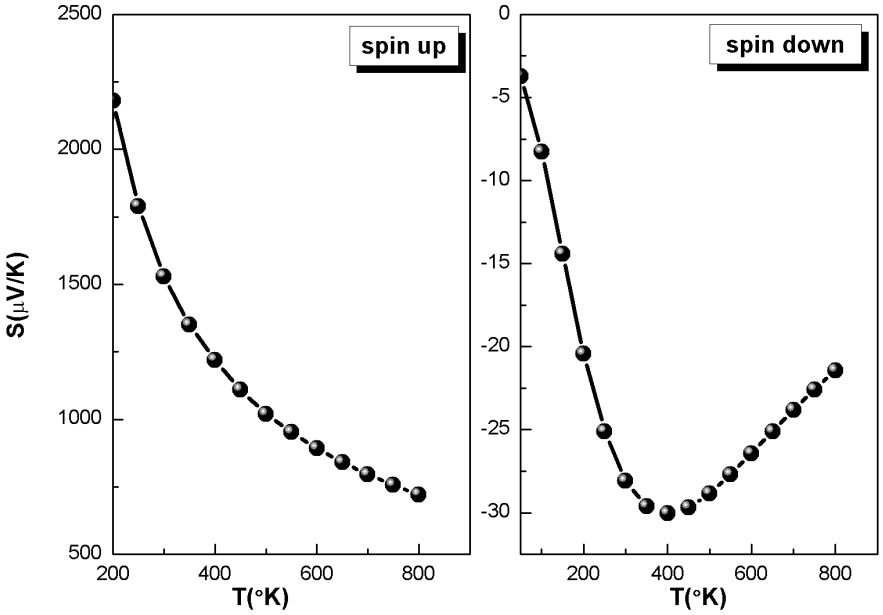

Fig. 5. The calculated Seebeck coefficient of 4H-GaN:Na-Na polytype versus temperature (a) Spin up state, (b) Spin down state.

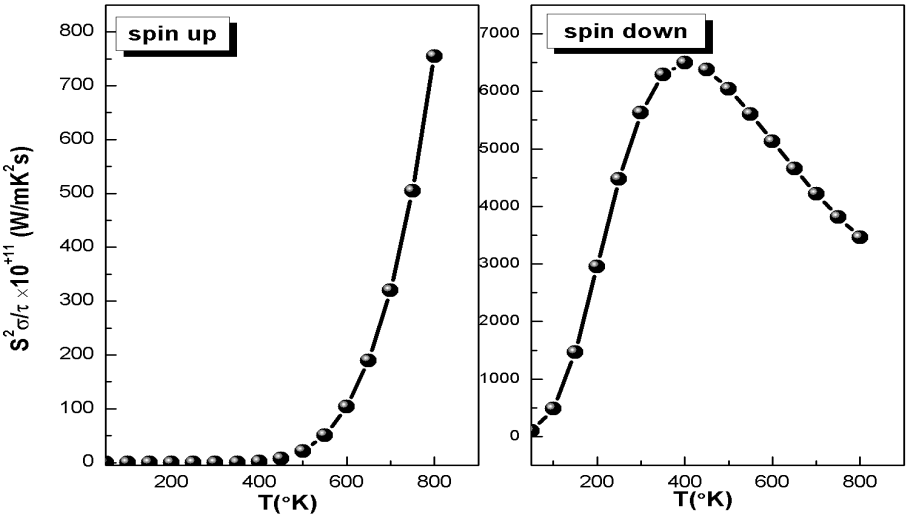

Fig. 6. The calculated Power factor of 4H-GaN:Na-Na polytype versus temperature (a) Spin up state, (b) Spin down state.

Figure 7(a-b) show the variation of ZT as a function of temperature for a fixed chemical potential ($\mu=E_F$= 4.8609eV) in both spin up and down states. The value of ZT increases with temperature in both spin up and spin down states. At the temperature of 400K, two peaks are detected having the value of 1.01to 400K and 0.03 respectively in spin up and down states. It is clear from these graphs that at 300K, ZT indicates a maximum value of 0.9943 and 0.0311 respectively for both spin configurations.

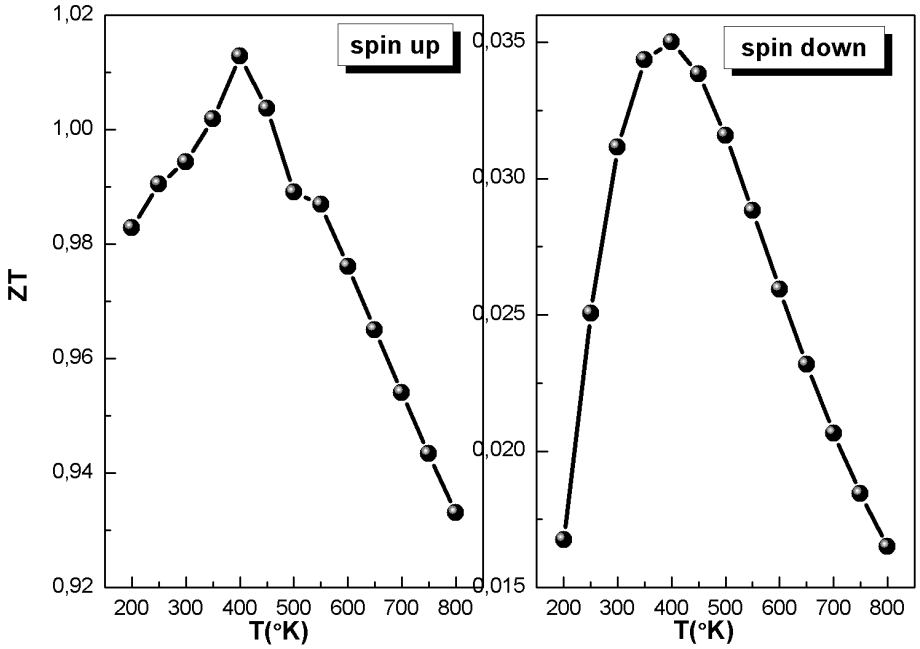

Fig. 7: The calculated graph of merit (ZT) of of 4H-GaN:Na-Na polytype versus temperature (a) Spin up state, (b) Spin down state.

CONCLUSION

The electronic and thermoelectric properties of (Na, Na) co-doped 4H-GaN polytype compound are computed using GGA within the framework of DFT. The calculation of the band structure reveals that4H-GaN:Na-Na is found to be half-metallic ferromagnetic. The thermoelectric properties of this compound are calculated for the first time in this work. Using the BoltzTraP code, electrical conductivity, beck coefficient, electronic thermal conductivity, electrical conductivity, electronic power factorand merit factor as function of temperature was obtained for 4H-GaN:Na-Na polytype. The ZT values found for this co-doped polytype at 400K temperature are 1.01 and 0.03 respectively for spin up and down states. We therefore expect these alloys to be potential candidates for the thermoelectric applications.

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