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Research Article

INVESTIGATION ON THERMOELECTRIC PROPERTIES OF WURTZITE ZnO USING MODIFIED BECKE JOHNSON POTENTIAL: A DFT STUDY

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A B S T R A C T

Based on Full Potential Linearized Augmented Plane Wave (FP-LAPW) method, we have investigated thermoelectric properties of zinc oxide in wurtzite phase. The exchange correlation effect is treated by employing modified Becke-Johnson (mBJ) potential coupled with Local Density Approximation (LDA). We have studied the thermoelectric properties of w-ZnO by calculating the transport coefficients such as Seebeck coefficient (S), electrical conductivity (σ/τ), thermal conductivity (κ_e/τ), thermoelectric power factor ($S^2\sigma/\tau$) and electronic figure of merit (ZT_e) within the constant relaxation time approximation. The present results elucidate that the undoped w-ZnO is a promising candidate for high temperature thermoelectric applications.

INTRODUCTION

A large fraction of energy produced throughout the world is lost as heat after consumption. It would be more appreciable if even a small percentage of this wasted energy is reused. In the recent years, the thermoelectric (TE) materials have attracted extensive interest in the field of research due to the rising demand for the energy conversion technologies. The TE materials can directly convert heat into electrical energy and vice versa, thus providing a substitute for power generation (Seebeck effect) and refrigeration (Peltier effect) [1,2]. The conversion efficiency of TE devices is characterized by the materials' thermoelectric figure of merit $ZT = S^2\sigma T/(\kappa_e+\kappa_L)$, where S is the Seebeck coefficient (potential difference between hot and cold ends of a material for unit temperature difference, i.e. S=dV/dT), σ is the electrical conductivity, T is the absolute temperature, κ_e and κ_L are the electrical and lattice contribution to the total thermal conductivity κ, respectively[3]. Hence the eventual approach to develop the conversion efficiency of a thermoelectric material is that its figure of merit (*ZT*) has to be increased. Ideally, to obtain a high *ZT*, both Seebeck coefficient and electrical conductivity must be increased, whereas thermal conductivity must be reduced. The *ZT* value for the conventional TE materials Bi_2Te_3, PbTe, $Si_{1-x}Ge_x$ is around 1 at their optimal temperature [1]. Therefore, a material with *ZT* value greater than or equal to unity can be utilized to make a good thermoelectric device.

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Most of the TE materials with high *ZT* value are expensive, rare or toxic elements. Therefore, materials which are economical, abundant and eco-friendly have been given much attention as possible alternativefor thermoelectric applications[4]. Though inter-metallic compounds are generally used as thermoelectric material, they are not stable at high temperatures in air. Thus, oxide-based thermoelectric materials have many advantages compared to the inter-metallic compounds, such as thermal stability, nontoxicity, oxidation resistance, etc. and can be expected to possess high performance[5].

Zinc oxide (ZnO) is one of the most promising semiconductor material of remarkable interest due to its wide direct band gap (3.37 eV), large exciton binding energy (60 meV), physical and chemical stability, biocompatibility, high photosensitivity and piezoelectric properties. Thus, it has wide range of technological applications in visible and ultraviolet light emitters, transparent field-effect transistors, ultraviolet nanolasers, photodetectors, solar cells, gas sensors and piezoelectric devices [6]. ZnO crystallizes in three different structures such as hexagonal wurtzite, cubic zincblende, and cubic rocksalt. Hexagonal wurtzite structure of ZnO is the most stable structure under ambient conditions, which belongs to the space group $P6_3mc$. The potential of ZnO as the thermoelectric material was recognized in 1996 by Ohtaki *et al.*[7]. Due to its tunable transport properties via doping, considerable studies have been reported on TE properties of ZnO,[8,9]. The effects of Al doping on the electronic structure and thermoelectric properties of the ZnO system have been reported by Jantrasee *et al.*[5]. Thermoelectric properties of rocksalt ZnO have been studied by Alvarado *et al.*[10] using

second-principles calculations. Though there are numerous works on thermoelectric properties of ZnO both experimentally as well theoretically, studies on TE properties of ZnO with mBJ potential are limited in literature. In the present work, we have investigated the thermoelectric properties of w-ZnO with the modified Becke-Johnson (mBJ) potential coupled with Local Density Approximation (LDA). The Boltzmann transport equation within the constant scattering time approximation is then used to calculate the transport coefficients such as Seebeck coefficient (S), electrical conductivity (σ/τ), and thermal conductivity (κ/τ). Finally we combine these results to evaluate the thermoelectric power factor ($S^2\sigma$) and the electronic figure of merit ZT_e.

Computational details

In the present work, we employed the full-potential linearized augmented plane wave (FP–LAPW) method to investigate the thermoelectric properties of w-ZnO within the frame work of Density Functional Theory (DFT) [11] as implemented in WIEN2k code [12]. To treat the exchange-correlation effect, the modified Becke-Johnson Local Density Approximation (mBJLDA) [13,14] is used. As the Perdew-Burke-Ernzerhof-Generalized Gradient Approximation (PBE-GGA)[15] underestimate the band gaps values of w-ZnO, the mBJLDA was employed to calculate the electronic and optical properties of w-ZnO in our previous work [6]. To attain the energy convergence of the eigenvalues, the wave function in the interstitial regions is expanded in plane waves with the cut off vector k_{max} and the value of k_{max} = 7.0/R_{MT} in the interstitial region. R_{MT} is the least muffin-tin radius and k_{max} denotes the magnitude of the largest *k*-vector in the plane wave expansion.G_{max} = 12 $Ry^{1/2}$ is the magnitude of the vector in charge density Fourier expansion and the value of angular momentum expansion is l_{max}=10.The R_{MT} values are 1.75 and 1.53 a.u. for Zn and O, respectively. The core cut off energy, which describes the valence and core states separation, was chosen as -6.0 Ry. The self-consistent calculations are iterated till the total energy converges below 10^{-4} Ry. Thermoelectric calculation requires a denser *k*-mesh for the convergence, and so a fine *k*-mesh (10000 k points)is chosen. The transport co-efficient of w-ZnO are calculated using the Boltzmann transport theory [16] as implemented in the BoltzTraP program [17] with modified Becke-Johnson Local Density Approximation (mBJLDA). The electronic structure input for BoltzTraP is adopted from the results of our previous work [6].

RESULTS AND DISCUSSION

The present study attempts to calculate thermoelectric properties of un-doped w-ZnO for the temperature range 100-1000K with mBJ potential. The band structures and partial densities of states are used to compute various thermoelectric parameters using BoltzTraP program [18].The calculated transport coefficients such as Seebeck coefficient (S), electrical conductivity (σ/τ), thermal conductivity (κ/τ), thermoelectric power factor ($S^2\sigma/\tau$) and electronic figure of merit (ZT_e) are shown in Fig. 1(a-e), respectively. Primarily, the core thermoelectric parameter, Seebeck coefficient S is calculated for ZnO and shown in Fig. 1(a). The value of S is very less for metals in the order of few μV/K whereas it is relatively higher for semiconducting materials [18]. The calculated Seebeck coefficient value for ZnO is marginally lesser than 250 μV/K below room temperature, but it remains ~250 μV/K in the temperature range 300K-1000K. The Seebeck coefficient is a sensitive parameter in understanding the band dispersion which is in relation with effective mass of either electrons or holes[19]. The considerably higher positive value of S indicates that ZnO is a p-type thermoelectric material with high effective mass for holes. This is due to the fact that the bands carrying holes after excitation are flatter (in forming a sharp DOS) around valence band maxima near E_F whereas the conduction band minima having electrons are more dispersive[6]. A negative value of S has been reported for ZnO by an experimental measurements [5,20], which can be justified by the fact that the ZnO samples are showing n-type semiconducting nature due to the presence of Zn interstitials and oxygen vacancies [21].

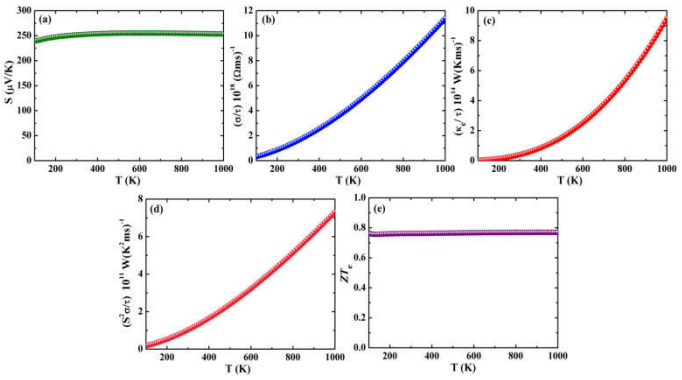

Fig 1 Variation of transport coefficients with temperature, (a) Seebeck coefficient (S), (b) electrical conductivity (σ/τ), (c) electronic thermal conductivity (κ_e/τ), (d) power factor ($S^2\sigma/\tau$) and (e) the thermoelectric figure of merit (ZT_e).

The variation of electrical conductivity (σ/τ) for ZnO is calculated and illustrated in Fig. 1(b). It shows marginally stronger dependence on temperature because of higher DOS below E_F, but the actual variations cannot be visualized due to the exclusion of the impact of temperature dependent relaxation time. It is well known that the thermal conductivity κ consists of lattice thermal conductivity (κ_L) and electronic thermal conductivity (κ_e). The κ_e can be expressed by the formula: $\kappa_e = L\sigma T$, $L = 2.45x10^{-8}$ $W\Omega K^{-2}$ is Lorentz constant, T is absolute temperature [10]. The electronic thermal conductivity (κ_e/τ) is calculated by using σ/τ and its variation with temperature is almost similar to σ/τ as shown in Fig. 1(c). The κ_e/τ value increases with the increasing temperature by the continuous production of electrons, but κ_L would decrease with temperature because of more phonon scattering at high temperatures and it will play a main role in the total thermal conductivity[22].

The thermoelectric power factor ($S^2\sigma/\tau$) and the electronic figure of merit (ZT_e) of w-ZnO are calculated and are shown in Fig. 1(d)-(e). Here, S and ZT_e are independent of relaxation time. Since S is almost constant in the considered temperature range, the nature of power factor curve resembles σ/τ. Since $ZT_e = S^2/L$, the electronic figure of merit is almost a constant value of ~0.76. However, the actual thermoelectric figure of merit *ZT* is also dependent on lattice part of thermal conductivity which is much more in magnitude than the electronic part for ZnO [20]. Since the lattice part of thermal conductivity κ_L involves different relaxation times, its calculation is very complicated and hence κ_L is not included in the present calculations. Thus, the calculated ZT_e for w-ZnO is overestimated compared to actual value since the calculation of ZT_e involving only κ_e/τ will yield considerably higher

values. If we include the lattice part, then the thermoelectric figure of merit *ZT* would be much lesser than 0.76.

CONCLUSION

We have performed a systematic computational study on transport properties of ZnO in wurtzite phase, by using the BoltzTraP code within the constant relaxation time approximation. Calculations are performed with mBJ potential coupled with LDA energy functional. The transport coefficients of the ZnO is a function of temperature are calculated. The calculated results show that the figure of merit ZT_e~0.76 in a wide temperature range of 200K to 1000K. The present results elucidates that w-ZnO can be used as potential thermoelectric material in a very desirable temperature range moderately above the ambient temperature.

References

1. X. Zhang, L.D. Zhao, Thermoelectric materials: Energy conversion between heat and electricity, *J. Mater.* 1 (2015) 92-105.
2. T. C. Harman, J. M. Honig, Thermoelectric and Thermomagnetic Effects and Applications, McGraw-Hill, New York., 1967.
3. C. Wang, Y. Wang, G. Zhang, C. Peng, Electronic structure and thermoelectric properties of ZnO single-walled nanotubes and nanowires, *J. Phys. Chem.* C. 117 (2013) 21037-21042.
4. D. P. Rai,Sandeep,A. Shankar, R. Khenata, A. H. Reshak, C. E. Ekuma, R. K. Thapa, San-Huang Ke, Electronic, optical, and thermoelectric properties of of $Fe_{2+x}V_{1-x}Al$, AIP Advances, 7(2017)451181-451188.
5. S. Jantrasee, P. Moontragoon, S. Pinitsoontorn, Thermoelectric properties of Al-doped ZnO: Experiment and simulation, *J. Semicond*. 37 (2016) 0920021-0920028.
6. Rita John, S. Padmavathi, Ab Initio Calculations on Structural , Electronic and Optical Properties of ZnO in Wurtzite Phase, Cryst. Struct. *Theory Appl*. 5 (2016) 24-41.
7. M. Ohtaki, T. Tsubota, K. Eguchi, H. Arai, High-temperature thermoelectric properties of $(Zn_{1-x}Al_x)O$, *J. Appl. Phys.* 79 (1996) 1816-1818.
8. M. Ohtaki, K. Araki, K. Yamamoto, High thermoelectric performance of dually doped ZnO ceramics, *J. Electron. Mater.* 38 (2009) 1234-1238.
9. J.P. Wiff, Y. Kinemuchi, K. Watari, Hall mobilities of Al- and Ga-doped ZnO polycrystals, Mater. Lett. 63 (2009) 2470-2472.
10. A. Alvarado, J. Attapattu, Y. Zhang, C. Chen, Thermoelectric properties of rocksalt ZnO from first-principles calculations, *J. Appl. Phys.* 118 (2015) 1651011-1651017.
11. W. Hohenberg, P. and Kohn, Inhomogeneous electron gas, *Phys. Rev.* B. 7 (1973) 1912-1919.
12. J. Blaha, P. Schwarz, K. Madsen, G.K.H., Kvasnicka, D. and Luitz, WIEN2k: An Augmented Plane Wave plus Local Orbitals Program for Calculating Crystal Properties. Technische Universität, Wien, Austria.
13. F. Tran, P. Blaha, Accurate band gaps of semiconductors and insulators with a semilocal exchange-correlation potential, *Phys. Rev. Lett*. 102 (2009) 5-8.
14. A.D. Becke, E.R. Johnson, A simple effective potential for exchange, *J. Chem. Phys.* 124 (2006) 2211011-2211014.
15. J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett*. 77 (1996) 3865-3868.
16. J.M. Ziman, Electrons and Phonons The Theory of Transport Phenomena in Solids, Oxford University Press, New York, (2001).
17. G.K.H. Madsen, D.J. Singh, BoltzTraP. A code for calculating band-structure dependent quantities, *Comput. Phys. Commun.* 175 (2006) 67-71.
18. R. Mohankumar, S. Ramasubramanian, M. Rajagopalan, M. Manivel Raja, S. V. Kamat, J. Kumar, Effect of Fe substitution on the electronic structure, magnetic and thermoelectric properties of Co_2FeSi full Heusler alloy: A first principle study, *Comput. Mater. Sci*. 109 (2015) 34-40.
19. J. Barth, G.H. Fecher, B. Balke, S. Ouardi, T. Graf, C. Felser, A. Shkabko, A. Weidenkaff, P. Klaer, H.J. Elmers, H. Yoshikawa, S. Ueda, K. Kobayashi, Itinerant half-metallic ferromagnets Co_2TiZ (Z=Si, Ge, Sn): Ab initio calculations and measurement of the electronic structure and transport properties, Phys. Rev. B - Condens. *Matter Mater. Phys*. 81 (2010) 1-20.
20. X. Qu, W. Wang, S. Lv, D. Jia, Thermoelectric properties and electronic structure of Al-doped ZnO, Solid State Commun. 151 (2011) 332–336.
21. K. Bandopadhyay, J. Mitra, Zn interstitials and O vacancies responsible for n-type ZnO: what do the emission spectra reveal?, *RSC Adv*. 5 (2015) 23540–23547.
22. W. Guan, L. Zhang, C. Wang, Y. Wang, Theoretical and experimental investigations of the thermoelectric properties of Al-, Bi- and Sn-doped ZnO, Mater. Sci. Semicond. *Process*. 66 (2017) 247-252.

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