Al Doped ZnO Thermoelectrics Determined from Electronic Structure

Rundong Wan (✉ rwan69@kust.edu.cn)

Kunming University of Science and Technology

Quanwei Jiang

Kunming University of Science and Technology - Lianhua Campus: Kunming University of Science and Technology

Zhengfu Zhang

Kunming University of Science and Technology - Lianhua Campus: Kunming University of Science and Technology

Sharon Kao-Walter

Blekinge Institute of Technology - Karlshamn Campus: Blekinge Tekniska Hogskola - Campus Karlshamn

Ying Lei

Anhui University of Technology

Guocai Tian

Kunming University of Science and Technology

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Abstract

For the aluminium doped wurtzite ZnO, comparing the Boltzmann transport theory calculated results and existing experiments, we acquire a few properties that are inaccessible otherwise. We find that the doping makes the samples metallic as the shifted Fermi levels are above the conduction band edge. We further find that the contradictory conclusions from two experiments with similar formula can be attributed to the quite disparate carrier concentrations and carrier mobility and the carrier mobility strongly relates to the sample preparation.

Introduction

As the climate change becomes severer, converting the wasted heat into electricity is very promising, except with an obstacle of low conversion efficiency. Thermoelectrics relies on the Seebeck effect, while a figure of merit ZT is used to describe the conversion efficiency. The ZT relates to other parameters through the equation $ZT = \sigma S^2 T / (\kappa_e + \kappa_l)$, where σ , S , T , κ_e , and κ_l are respectively the electrical conductivity, Seebeck coefficient, temperature, electronic thermal conductivity, and lattice thermal conductivity.¹⁻³ High electrical conductivity and high Seebeck coefficient cannot coexist in a natural material. Furthermore, the electronic thermal conductivity is linear to the electrical conductivity, indicating the high electrical conductivity might cause high thermal conductivity.⁴⁻⁶ There have been extensive studies on how to optimize thermoelectric performance.

The wurtzite ZnO is a large bandgap semiconductor, which should have large Seebeck coefficients and low electrical conductivities. Due to its potential high-temperature thermoelectric applications, there have been extensive studies on the aluminum-doped ZnO to increase the electrical conductivity, started by Ohtaki et al.⁷ Cai et al obtain Al-doped ZnO samples by hot pressing ZnO–Al₂O₃ powder to improve σ by two orders.⁸ Jood et al find that the Al-induced grain refinement ZnAl₂O₄ nanoprecipitates presages lead to $\kappa \sim 2 \text{ Wm}^{-1} \text{ K}^{-1}$, $\alpha \sim -300 \mu\text{V K}^{-1}$ and $\sigma \sim 1 \cdot 10^4 \Omega^{-1} \text{ m}^{-1}$ at 1000 K.⁹ However, with the same formula Al_{0.01}Zn_{0.99}O, the RF plasma processing¹⁰ and codepositing¹¹ yield samples are quite discrepant in terms of Seebeck coefficient. This is very confusing. Another difficulty is that Ohtaki et al and Cheng et al both claim the samples are metallic because of the high electrical conductivity.^{7, 10} The large bandgap ZnO becoming metallic seems unrealistic, while the semiconducting-metallic transition needs are proved rigorously from the Fermi level perspective. When a Fermi level is above the conduction band minimum (CBM), the material is metallic. Nevertheless, theoretically calculating a Fermi level for a doped model is very challenging, as the calculation may involve 100 atom supercell of many configurations.

Here, we adopt a different approach. We use BoltzTraP2 to solve the BTE when we adopt the rigidband approximation (RBA).¹² In the approximation, the band structure is not changed, even with doping or heating. This would lead to tremendous savings because we only use the band structure of the pure unit cell, rather than a supercell approach adopted in a first principle study considering the doping levels. The Fermi energy and carrier concentrations are a function of doping level and temperature, i.e. the doping

effect is incorporated within the varying Fermi level. The bandgap will not change, but for an n-type semiconductor, the Fermi level shifts toward the conduction band. When the carrier concentration is not too high and the doping does not introduce impurity states in the bandgap region, the RBA is valid, proven by the success of BoltzTraP2 application in thermoelectric materials.

By comparing with the experimental results, we retrieve the related properties. We find that all the Fermi levels are indeed above the CBM, showing the semiconducting-metallic conversion. We also find that the unexpected high Seebeck coefficients come from the low carrier concentrations. We analyze why different processing of giving different carrier concentrations.

Computational Details

We study a unit cell of 4 atoms. ZnO has a typical wurtzite structure and the lattice constants are $a = b = 3.29 \text{ \AA}$ and $c = 5.30 \text{ \AA}$ with $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$, respectively. We perform the geometry optimization of the unit cell with VASP, choosing the recommended settings.^{13–16} We do not consider the electron spin, because its effect on the thermoelectrics is negligible. We use Perdew-Burke-Ernzerhof (PBE) to exchange-correlation functions for geometric optimization and energy calculation. In the energy calculation,¹⁷ we set the following parameters: cut-off energy 520 eV (1.3 times larger), total frequency band 22, and kmesh $18 \times 18 \times 9$. Using the resulting charge file, we calculate the density of states (DOS) with a denser $42 \times 42 \times 21$ kmesh, while other settings are the same as in the energy calculation. We use a modified BeckeJohnson (mBJ) function to get the DOS file. The DOS file is the input for subsequent BoltzTraP2 calculations to solve the electronic Boltzmann transmission equation.¹⁸ The BoltzTraP2 interpolation magnifies the kmesh by 30 times. Using the generated BT2 file, we perform the integration throughout the configuration space. The data is then extracted from the trace file.

Results

The optimized geometry of P63mc wurtzite ZnO has lattice constants of $a = b = 3.29 \text{ \AA}$ and $c = 5.30 \text{ \AA}$ with $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$, respectively, in a precise agreement with the experimental values. The experimental bandgap of 3.4 eV is difficult to reproduce by conventional first principle studies, which is normally about 1.1 eV. This difference would cause severe estimation error at high temperatures, as bipolar effects occur for a narrow bandgap semiconductor of 1.1 eV bandgap, whereas the much large bandgap would suppress such effect. We use different CMBJ values of 0.225 and 1.008 to obtain 3.37 eV of the bandgap. The bandgap from other functions can be adjusted to this value, but the mBJ might yield good bands shape that is important in determining thermoelectrics. It is a direct bandgap semiconductor, with a sharp nongenerate parabolic conduction band. Though the initial Fermi energy locates near the top of valence bands for a pure model at absolute zero degrees Kelvin, the doping and heating change the Fermi levels.

According to the first experimental data,¹⁰ the maximum Fermi level and minimum ones are respectively 0.68 eV and 0.41 eV above the CBM shown in Fig. 1, which have a window of 0.27 eV. They are all above the CBM, meaning that the doping changes the larger bandgap ZnO into metallic due to very heavy doping. The lowest Fermi level and the highest one are respectively at 325K for $x = 0.04$ and at 1025 K for $x = 0.02$. This is against normal thermoelectric materials because Fermi energy is a function of temperature and doping level. As the doping level increase, the Fermi level increase, whereas the opposite trend occurs with the temperature change. Another abnormality is that the big span of Fermi energies should cause a large variety of carrier concentration, which will be shown later. The higher than the CBM unambiguously demonstrate the metallic behavior from the electronic structure perspective.

For the second experimental data,¹¹ the maximum and minimum Fermi levels are respectively 0.14 eV for $x = 0.01$ at 773K and 0.38 eV for $x = 0.03$ at 1073 K above the CBM. These two doping cases become metallic substantially, as for an electron, the room-temperature thermal energy is about 0.025 eV. If we adopt the FermiDirac distribution, the carrier concentration should be enormously large. We also notice with the same molecular formula $\text{Al}_x\text{Zn}_{1-x}\text{O}$, for $x = 0.01$, the Fermi energies have at least 0.26 eV difference, which is huge.

With the existing experimental temperature-dependent Seebeck coefficient $S(T)$, at each temperature, we search the calculated Seebeck coefficients around the experimental one. In our experience, there are similar values close to each other, but the carrier concentrations N_s are sometimes quite disparate. Therefore, putting $N(T)$ as a checking tool by ensuring its smoothness. We acquire the corresponding $S(T)$. In the process, the temperature dependence of the Fermi level, electronic DOS, electrical conductivity per relaxation time, Hall coefficient, and electronic thermal conductivity per relaxation time are obtained. Using these calculated properties and experimental $\sigma(T)$, we can obtain other inaccessible properties by an experiment or a calculation alone.

Corresponding to the experimental results, we obtain the $N(T)$ solidline curves, shown in Fig. 2. For the first experiment, all $N(T)$ increase, which indicate a semiconductor behavior though the Fermi energies indicate metallic nature. These curves do not obey the metallic FermiDirac distribution since the Fermi levels are above the CBM, but the curvatures behave like semiconductors' FermiDirac distribution. The carrier concentration can change from 2.86 to 9.22 (10^{20} cm^{-3}), which are by themselves very large and have an unexpectedly large range. Though $x = 0.01$ demonstrates the saturated carrier concentrations at most the temperatures, the $x = 0.02$ $N(T)$ curve shows different behavior, which can be attributed to the spinel ZnAl_2O_4 existence. All $N(T)$ curves undergo drastic change as high as 2.56 times, indicating there is a mechanism constraining the electrons from being conductive. The wurtzite ZnO is a special oxide as it has both ionic and covalent bonding, which comes from the sp^3 orbital hybridization.¹⁹ When an aluminum atom substitutes a zinc atom in the ZnO, the extra electron contributed by the aluminum cations is Coulomb attracted by the surrounding Zn cations. With the rising temperature and consequent thermal energy, the electron can gradually unshackle from the trap. For the latter experiment, the $N(T)$ curves are considerably lower. Nevertheless, the room temperature carrier concentrations are respectively

1.72 and 1.88 (10^{19} cm^{-3}) for $x = 0.01$ and $x = 0.03$, while these carrier concentrations still indicate heavy doping. The experimental sample preparation method by chemical deposition must cause structural difference RF plasma one, because of quite different Fermi energies and carrier concentrations despite similar doping levels. The electrons contributed by aluminum are further so strongly constrained by the surrounding Zn cations that only at 973 K, the thermal energy frees the electron from the trap.

One can measure a carrier concentration experimentally with the Hall method. We check the applicability using the formula $r = N \cdot q \cdot R_h$, where r , q , and R_h are the Hall factor, carrier charge, and Hall coefficient, respectively. We find that the r factor is essentially 1.0, the widely used constant in the literature. The reason is that we have one single parabolic conduction band at the Γ . For the n-type ZnO, all other bands are far away, even we integrate over the bands around the Fermi level. The single parabolic band is the foundation for the success of the Hall Effect.

The temperature-dependent electrical conductivity per relaxation time is shown in Fig. 3a. The trend of curves is remarkably similar to that of the $N(T)$ curves. Given the constant relaxation time and electronic mobility, the electrical conductivity should be linear with the carrier concentration.

Even though the carrier concentrations of the 2nd experiment are one order lower than those of the 1st one, the electrical conductivities are a few times lower. This comes from different scattering mechanisms. Using the calculated electrical conductivity per relaxation time σ/τ , the experimental electrical conductivity σ , and the formula $\tau = \sigma_{\text{exp}}/(\sigma/\tau)_{\text{cal}}$ at each experimental temperature, we arrive at $\tau(T)$, which describes the relaxation time as a function of temperature. We show the $\tau(T)$ patterns in Fig. 3b. For the 1st experiment, the three lower $\tau(T)$ curves look similar to tellurium doped CoSb₃ in terms of the size and trend, which indicates an acoustic phonon scattering dominance with inverse temperature dependence. For the 2nd experiment, the relaxation times span from 14.4 to 1.35 fs in a steep decline. With much fewer carrier concentrations, the much lesser relaxation makes it up for the electron conductivity until very high temperatures. This might be attributed to the sample preparation again. In many thermoelectric materials, the acoustic phonon scattering dominates. With the ZnO, the polar optical phonon scattering might contribute to the rising relaxation time. Another scattering such as ion scattering, vacancy scattering, and non-polar optical phonon scattering should diminish at high temperatures. The sharp decrease in the relaxation time of the 2nd experiment is unknown.

The relaxation time reflects the obstacles encountered by a moving electron, while this cannot be visualized directly. The electronic mobility offers a more intuitive picture. Using the experimental electrical conductivity σ , the carrier concentration N , and the equation $\sigma = Ne\mu$, where μ is the mobility, we have a μ . The temperature dependence $\mu(T)$ curves are shown in Fig. 3c. The pattern looks similar to that of $\tau(T)$ curves as these two quantities are linear if the electron mass is unchanged. For the 2nd experiment, the mobility can reach 40 cm^2/Vs , while the undoped ZnO has an electron mobility of 200 cm^2/Vs . The high mobility of the 2nd experiment explains the lower but moderate electrical conductivity.

The calculated and experimental temperature-dependent Seebeck coefficient is shown in Fig. 4. For the 1st and 2nd experiments, the size difference is striking, given the similar doping levels. Because the calculated $S(T)$ curves are in good agreement with the experimental ones and the calculated ones have much lower carrier concentrations for 2nd experiment, the low carrier concentration leads to a high Seebeck coefficient. Those much lower carrier concentrations are the reason why in the 2nd experiment, the doped $S(T)$ curves are proximate to the one of pure ZnO. When we have high a Seebeck coefficient, a moderate electrical conductivity, and the corresponding temperature, we have a high power factor, defined as $PF = \sigma S^2 T$, which is an important indicator of thermoelectric performance. Based on the above observations, we conclude that the high Seebeck coefficient and high electrical conductivity are not mutually exclusive. When we have a low carrier concentration, we have a high Seebeck coefficient. If a material has a high relaxation time or high carrier mobility, the material would have a high electrical conductivity. This way, we may obtain a good thermoelectric material. Synthesizing this kind of material becomes the key, while the co-deposited $Al_xZn_{1-x}O$ ($x = 0.01$ and 0.03) seem to achieve this goal until 673 K, after which the Seebeck coefficients plummet sharply, reducing the high-temperature performance. This trend is against the typical large bandgap semiconductor behavior that has to learn $S(T)$ curves. The sharp decrease of $S(T)$ curves for the 2nd experiment is due to the sharp increase in the carrier concentration after 673 K. The $S(T)$ curves of the 1st experiment are consistent with large bandgap semiconductor whereas the ones of the 2nd are not.

Achieving a high power factor only fulfills part of success, while we also need a low thermal conductivity as low as $3 \text{ W/m}\cdot\text{K}$. We calculated the electronic contribution to the thermal conductivity, while the calculation of the lattice contribution involves solving phonon BTE, which needs a different package. We focus on the electrical part and estimate the lattice contribution to be the difference between the experimental total one and the calculated electronic one. The temperature dependence is shown in Fig. 5a. While the experimental κ can reach $5 \text{ W/m}\cdot\text{K}$ for the 2nd experiment, this does not yield a final good thermoelectric performance as the Seebeck are substantially lower. The electronic contribution to the thermal conductivity is negligible in each doping, which indicating the tuning of the lattice contribution is decisive.

Discussion

A Fermi energy can determine intuitively whether the aluminum-doped wurtzite ZnO becomes metallic, but theoretically estimating the Fermi energy is difficult. For the undoped model, the Fermi level locates in the bandgap region. In any ab initio calculation, we need to build a supercell of a much large number of atoms. For $x = 0.01$ doping, a supercell has 100 atoms and many configurations, from which we need to find the one with the maximum formation energy. For each configuration, we search for the most stable structure, which consumes a huge amount of time. Using the RBA in BoltzTraP2, we tremendously reduce such burden, because we only consider the pure unit cell of ZnO. This concerns 4atom electronic structure, which can be calculated quickly and easily. On this calculated electronic structure, the calculation of varying Fermi levels is straightforward. As a Fermi level is a function of doping level and

temperature, we can obtain them conveniently by comparing it with an experiment. For each of the doped case, the Fermi level is above the CBM, displaying that all $\text{Al}_x\text{Zn}_{1-x}\text{O}$ become metallic.

For the same formula $\text{Al}_{0.01}\text{Zn}_{0.99}\text{O}$, why the 1st and 2nd experiments give quite different Seebeck coefficients is that the carrier concentrations are quite different. Consequently, the Fermi levels, electrical conductivities, relaxation times, mobilities, and electronic thermal conductivities are quite different. Different syntheses constrain the conduction electrons differently because of the microstructure, where zinc cations play an important role.

We can obtain a high electrical conductivity and a high Seebeck coefficient simultaneously if we have a low carrier concentration and high carrier mobility. Codepositing components could achieve this goal shown in the 2nd experiment, while the instability at high temperature destroys the potential, as the mobility decreases sharply, and the carrier concentration increase sharply, leading to the steeping plummet of the Seebeck coefficient.

In the experiments, powders are used, while we assume a single crystal. The calculated results show that in the experimental temperature range, the thermoelectric coefficients are isotropic. Furthermore, we use the averaged values instead of vectors or tensors. The experimental powder should help to reduce the lattice thermal conductivity, but not the electronic properties, when the grains are not tiny enough to affect electrical structure.

Conclusions

The changed Fermi levels of aluminum-doped wurtzite ZnO indicate that the doping makes the sample metallic, which is unexpected because of the large bandgap. The RF plasma processing and codepositing give similar molecular formula but quite disparate microstructures that constrain conduction electrons quite differently, yielding striking lower carrier concentration for the latter one. The co-deposited ones have a similar Seebeck coefficient to the pure ZnO and much higher mobility and subsequent moderate electrical conductivity. This gives the co-deposited samples good thermoelectric performance until 673 K when the performance plummets. To have good thermoelectric material, the Seebeck coefficient and electrical conductivity need to be both high by having a low carrier concentration and high mobility.

Declarations

Conflicts of interest

There are no conflicts to declare.

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Figures

Figure 1

Electronic band structure of ZnO calculated by mBJ functional. Dotted lines for the new Fermi level of $\text{Al}_x\text{Zn}_{1-x}\text{O}$

Figure 2

Temperature dependence of Carrier concentration N , where I and II denote the 1st and 2nd experiment, respectively.

Figure 3

Temperature dependence of (a) electrical conductivity per relaxation time (σ/τ), (b) the relaxation time (τ) and (c) the mobility (μ).

Figure 4

(a) Calculated and experimental temperature-dependent Seebeck coefficient as a function of temperature. The solid figure represents the calculation data, and the hollow figure represents the experimental data.

(b) DOS effective masses as a function of temperature.

Figure 5

Temperature dependence of the thermal conductivity, where the high solid lines represent the experimental total and the low dotted ones are for the electronic contribution. The lattice contribution are the differences.