Thermoelectric Transport Properties of Naturally Nanostructured Ga-ZnO Ceramics: Effect of Point Defect and Interfaces

Xin Liang*

School of Engineering and Applied Sciences, Harvard University, Cambridge,
Massachusetts 02138, United States

Abstract

Point defects and nanoscale interfaces have been found of significant influence on the phonon and electrical transport properties. In the preset work, we present the high temperature thermoelectric properties of naturally nanostructured Ga-ZnO ceramics synthesized by sparking plasma sintering process. By varying the GaO_{1.5} doping concentration, compositionally dependent structures were formed, from point defected solid solution to nanostructures with superlattices and nanotwins. The introduction of low GaO_{1.5} concentration increases both electron and point defect concentrations, leading to significantly increased electrical conductivity while reduced thermal conductivity. The nanostructure interfaces are found to increase scattering of both charge carriers and phonons, leading to drastically reduced electronic mobility and lattice thermal conductivity. A combined analysis of electrical conductivity and Seebeck coefficient with temperature was also developed, which revealed that the dominant electron scattering

* Corresponding author: liangxin@cczu.edu.cn (X. Liang) ; now at School of Materials Science and Engineering, Changzhou University, Changzhou, Jiangsu 213164, China

mechanism changes with defect concentration. We believe that this approach is also likely applicable to other thermoelectric material systems.

Keywords: ZnO; Nanostructure; Thermoelectrics; Seebeck coefficient

Introduction

Thermoelectricity has emerged as a sustainable energy conversion approach and attracts intensive research efforts. ZnO based materials, with the merit of oxides on chemical inertness and stability, have gained practical importance in high temperature thermoelectric applications. In addition, unlike classic thermoelectric materials such as PbTe with high toxicity and cost, ZnO is an earth abundant and environmental friendly material with controllable electrical conductivity. Thermoelectric property is commonly characterized by the figure of merit (ZT), defined as $S^2\sigma T/\kappa$, where S , σ , κ and T represents Seebeck coefficient, electrical conductivity, thermal conductivity and absolute temperature. Clearly, increasing the electrical conductivity and reducing the thermal conductivity is central to improve the thermoelectric properties.

Numerous efforts have been made on improving thermoelectric properties of ZnO, by electron doping with elements such like Al³⁺^{1, 2, 3, 4} and In³⁺^{5, 6, 7}. Ga³⁺ doping has also been applied to enhance the electrical conductivity of ZnO^{8, 9, 10}, while there is few studies reported on the consequent thermoelectric transport properties, especially on the thermal conductivity and Seebeck coefficient. In addition, unlike lightly doped ZnO, Ga-enriched ZnO also possesses complex nanostructures. It has been reported^{11, 12, 13, 14, 15} that homologous Ga₂O₃(ZnO)_k natural superlattice structures exists, especially in the Ga

highly doped ZnO, in which k is an integral number basically denoting the number of Zn-O layers between Ga-O layers. Such superlattices belongs to the $\text{RMO}_3(\text{ZnO})_k$ type of homologous layered oxides^{11, 16, 17, 18, 19}, and very low thermal conductivity can be expected due to the phonon scattering by the Zn(Ga)-O/Ga-O nanoscale interfaces, which is important to achieve high thermoelectric performance.

Nevertheless, a search of literature reveals that, research on Ga doped ZnO mostly concentrates on the electrical and optical properties^{8, 15, 20}, few attempts have been made either on measuring the Seebeck coefficient or evaluating the thermal conductivity. In addition, no ZnO-Ga₂O₃ binary phase diagram exists to our knowledge which can be a useful guide to engineer the phase composition and microstructure. The absence of research on investigating the thermoelectric properties of Ga-ZnO ceramics stimulates us to conduct the present work.

In this paper, we reported the high temperature thermoelectric properties of Ga-ZnO ceramics synthesized by wet chemistry and sol-gel combustion approach, and solidified by spark plasma sintering. We characterize the compositionally dependent defect structures and investigate the effect of point defects and interfaces on thermoelectric transport properties. In the Ga enriched ZnO, we observed the naturally formed $\text{Ga}_2\text{O}_3(\text{ZnO})_k$ superlattice compounds and the nanotwins as well. We found that these nanoscale interfaces provides additional strong phonon scattering, leading to the drastic reduction in thermal conductivity. We developed and applied a semiconductor physics model on our electrical conductivity and Seebeck coefficient measured with temperature. In doing so, we estimated the Fermi level and the dominated electron scattering mechanism in each Ga doped ZnO.

Experiments

The Ga doped ZnO oxide powders were prepared using a wet chemistry gel combustion method. The commercial high purity nitrate powders, $\text{Zn}(\text{NO}_3)_2$ (99.999%, Sigma Aldrich® , USA) and $\text{Ga}(\text{NO}_3)_3$ (99.999%, Sigma Aldrich® , USA), were prepared in solutions in distilled and deionized water. After the ionic concentration was determined, two solutions were mixed together according to the designated Ga concentration of 18 atomic percent. The mixed solutions were uniformly stirred and heated and kept at 80 °C, followed by the addition of several organic fuels (acrylamide, N,N'-Methylene-bisacrylamide, 2,2'-Azobisisobutyro-nitrile and ammonium persulfate) which converted the liquid into gel. After being dried in a low temperature oven at 120 °C for 12 hours, the dehydrated gel was crushed into small pieces and sent to combustion furnace where self-assisted reaction occurred at about 600 °C. The residual powders after reaction, which were mainly mixture of oxide powders and carbon, were then calcined at 800 °C for 2 hours. The calcined powders were sintered into solid pellet of 12.7 mm in diameter and ~ 1.00 mm in thickness using our home-made current assisted densification processing system (also known as spark plasma sintering) at 900 °C for 5 min. The entire sintering process was under vacuum and with a constant compressive stress of 125 MPa. The sintered sample was annealed at 1000 °C in air for 2 hours to compensate the oxygen deficiency, followed by a thermal treatment of 1150 °C for 1 day. During the post-annealing, samples were wrapped by the oxide powders of the same composition and kept in a closed crucible to minimize the evaporation of ZnO. As reference, pure ZnO solid pellet was also made from high purity commercial powders

(99.999%, Sigma Aldrich® , USA) using the same method and also post-annealed at 1150 °C for 1 day.

X-ray diffraction data were recorded at a Bruker® D8 Discover Diffractometer and the phase compositions were analyzed using 2011 ICDD PDF database . Raman spectroscopy was performed on a LabRAM Aramis Raman system (Horiba Jobin Yvon, Edison, NJ) using the 532 nm excitation laser operated at room temperature. The Raman spectra were collected with a 10 µm diameter laser beam on a sufficiently large area to acquire the global information. The recorded spectra were post-analyzed using a commercial software package (GRAMS, Thermo Electron Corp., Philadelphia, PA). Each spectrum was calibrated by monitoring the laser Rayleigh line at 0 cm⁻¹.

For preparing transmission electron microscopy (TEM) observations, both sides of the specimen were mechanically polished till the thickness was reduced to 60 – 80 µm, followed by ion beam milling on a Fischione® 1010 Dual Beam Ion-Mill machine. The specimen was further cleaned on a Fischione® 110 Plasma Cleaner and the high resolution TEM investigations were made on a JEOL® 2010 FEG-TEM.

Thermal conductivity (κ) was determined from the measurement of thermal diffusivity (α), mass density (ρ) and heat capacity C_p , using the following relation

$$\kappa(T) = \alpha(T) \cdot \rho \cdot C_p(T) \quad (1)$$

in which the thermal diffusivity was measured from room temperature to 800 °C in flowing Argon gas on a NETZCH Micro Flash® LFA 457 instrument. Mass density was obtained using Archimedes method and the heat capacity with temperature was calculated using the Kopp-Neumann rule from literature data ²¹. The specimen was cut

into the bars of $2 \times 2 \times 8$ mm dimensions for electrical conductivity and Seebeck coefficient measurements, which were made from room temperature to 800 °C in air on a ULVAC RIKO® ZEM 3 M10 unit.

Results

The mass density of the sintered samples is reduced with the addition of $\text{GaO}_{1.5}$, measured as 5.579, 4.815, 4.982 and 4.871 g/cm³ for pure ZnO and 2, 4 and 18 mol. % $\text{GaO}_{1.5}$ doped ZnO samples. X-ray diffraction results of all the samples annealed at 1150 °C for 1 day are presented in Figure 1, with the characteristic peaks of identified phases indicated at the bottom. Unlike ZnO with hexagonal structure, the ZnGa_2O_4 spinel phase has a cubic structure (ICDD# 00-038-1240). It has a few X-ray diffraction peaks which are most distinguishable from ZnO in the present scan range, as indicated by the red dashed lines. The 2 mol. % $\text{GaO}_{1.5}$ doped ZnO basically has the ZnO solid solution phase without the formation of ZnGa_2O_4 spinel phase. However, apparent broadening of ZnO (103) peak (2θ at about 63 degree) was observed, suggesting the presence of fine structures, which are possibly nanotwin boundaries which has been reported in the 2 mol. % $\text{GaO}_{1.5}$ doped ZnO¹³. In the 4 mol. % $\text{GaO}_{1.5}$ sample, in addition to the ZnO solid solution phase, a homologous superlattice phase $\text{Ga}_2\text{O}_3(\text{ZnO})_9$ was also formed which has the orthorhombic structure (ICDD# 00-050-0448); no ZnGa_2O_4 spinel phase was found in this sample. Both $\text{Ga}_2\text{O}_3(\text{ZnO})_9$ superlattice structure and ZnGa_2O_4 spinel phase were identified in the 18 mol. % $\text{GaO}_{1.5}$ doped ZnO where $\text{Ga}_2\text{O}_3(\text{ZnO})_9$ has a dominant phase fraction.

Figure 1: X-ray diffraction data of Ga doped ZnO after 1150 °C 1 day thermal treatment. The characteristic peaks of $\text{Ga}_2\text{O}_3(\text{ZnO})_9$, ZnGa_2O_4 spinel and ZnO phases are shown at the bottom of the figure. A few of most distinguishable ZnGa_2O_4 spinel peaks are also indicated by the vertical dashed red lines.

Raman spectra of all the samples are presented in Figure 2, with characteristic Raman modes of ZnO ²² and ZnGa_2O_4 ²³ structure indicated on the spectra represented by

the labels or dashed lines of olive and red colors, respectively. With increasing gallium addition, the Raman spectrum basically remains most of the ZnO characteristic Raman modes, whereas a systematic broadening and shift of ZnO Raman modes such as E_2 modes at 101 and 438 cm^{-1} were observed. Characteristic Raman modes of ZnGa_2O_4 spinel structure with notation of “s” are labeled on the figure according to Van Gorkom *et al*’s report ²³; however, both T_{2g} at 611 cm^{-1} and E_g mode at 636 cm^{-1} were not observed by Preudhomme and Tarte ²⁴, and there was also discrepancy between two references on whether the T_{1u} mode position is at 570 or 593 cm^{-1} . However, both peaks at 577 cm^{-1} and 636 cm^{-1} , although with much reduced Raman intensity, were also observed in both 2 and 4 mol. % $\text{GaO}_{1.5}$ doped ZnO samples, in which the spinel phases were not detected by X-ray diffraction. In addition, these Raman peaks appear much broader than those reported in the literature ²³.

Figure 2: Raman spectra of Ga doped ZnO annealed at 1150 °C for 1 day; pure ZnO data was also enclosed. The characteristic Raman modes for ZnO and ZnGa₂O₄ spinel phase are indicated by olive and red colored labels, respectively. Raman modes of interests in the present work are also indicated by the dashed lines across all the spectra.

The homologous superlattice structures Ga₂O₃(ZnO)₉ revealed by high resolution TEM are shown in Figure 3, where nanotwin nanostructures were revealed. The twinning relationship with a crystallographic angle of 60° was clearly characterized from both the

image and the corresponding diffraction pattern as shown in Figure 3 (b); this is consistent with literature findings that twin boundaries in Ga doped ZnO are on $\{01\bar{1}3\}$ planes of ZnO^{12, 13}. The diffuse streaks of superlattice reflection spots corresponding to the planar faults or interfaces were also observed in the electron diffraction pattern. In addition, the nanotwin boundary spacing is found to vary with locations, but has a typical length scale of 2 ~ 5 nm.

Figure 3: HRTEM image (a) and the corresponding diffraction pattern (b) of superlattice structures with nanotwins in 18 mol. % GaO_{1.5} doped ZnO. The HRTEM image reveals the nanotwin boundary with a crystallographic angel of about 60 °. The electron diffraction pattern was taken along the $[\bar{1}2\bar{1}0]$ direction, which consists of two sets of lattices; in addition, diffuse superlattice reflection streaks were also observed.

Measured thermal conductivity of Ga doped ZnO from room temperature up to 800 °C are presented in Figure 4. Also shown are the data of undoped ZnO for comparison. All the samples presented here were annealed at 1150 °C for 1 day. A significant reduction of thermal conductivity was observed even with a 2 mol. % GaO_{1.5}

addition. With increasing addition of $\text{GaO}_{1.5}$, the thermal conductivity decreases and the temperature dependence is drastically reduced. As seen on the figure, the thermal conductivity of 18 mol. % $\text{GaO}_{1.5}$ doped ZnO is virtually independent on temperature. Electrical conductivities measured with temperature up to 800 °C are shown in Figure 5. All the Ga doped ZnO have much improved electrical conductivity than the undoped ZnO, and the 2 mol. % $\text{GaO}_{1.5}$ doped ZnO demonstrates highest electrical conductivity whereas the 4 and 18 mol. % $\text{GaO}_{1.5}$ doped ZnO samples have similar values in the temperature range measured.

Figure 4: Thermal conductivity measured with temperature for Ga doped ZnO samples with data of undoped ZnO shown for comparisons, represented by scattered symbols. All the samples presented on this figure were annealed at 1150 °C for 1 day. The lines through the data points are the least square fit.

Figure 5: Electrical conductivity of Ga doped ZnO measured with temperature up to 800 °C. Pure ZnO data are also indicated. The lines through the data points are the least square fit.

Figure 6 presents the Seebeck coefficient measured with temperature; detailed description of Seebeck coefficient analysis will be given in the later content. Across the entire temperature range of measurements, all the samples studied were found to be n-type semiconductors as seen from their negative values of Seebeck coefficient. Also, Seebeck coefficients of all the Ga doped ZnO samples studied generally increase with temperature.

Figure 6: Seebeck coefficient of Ga doped ZnO measured with temperature up to 800 °C. The experiment results are shown as scattered symbols, and the modeling fits of the measured data for extracting the information on the dominant electron scattering mechanism are represented by dashed lines with the same colors of the measurement data symbols.

Discussions

Solid Solution and Nanostructures of Ga doped ZnO

It is unambiguous from the combined results of X-ray diffraction and Raman spectroscopy that there are $\text{Ga}_2\text{O}_3(\text{ZnO})_9$ like homologous superlattice structures and ZnGa_2O_4 spinel phase (may also be with a small amount of ZnO solid solution phase) present in the 18 mol. % $\text{GaO}_{1.5}$ doped ZnO. The X-ray diffraction results clearly exclude the presence of spinel phases in both 2 and 4 mol. % $\text{GaO}_{1.5}$ doped ZnO samples. However, the broad Raman peaks at 577 and 636 cm^{-1} , which were assigned to T_{1u} and E_g modes of ZnGa_2O_4 spinel phase by Van Gorkom *et al.*²³, were observed in all the three

Ga doped ZnO samples as seen in Figure 2. It is in question whether they arise from the ZnGa₂O₄ spinel structure, considering that T_{2g} mode at 611 cm⁻¹ and E_g mode at 636 cm⁻¹ were not observed by Preudhomme and Tarte²⁴ as well as a non-negligible discrepancy on the peak position of Raman mode at 577 cm⁻¹. It is not impossible in both references^{23, 24} that homologous superlattice compounds Ga₂O₃(ZnO)_k formed and some of their Raman modes were mistakenly assigned to the ZnGa₂O₄ spinel phase such as those at 577 and 638 cm⁻¹ by Van Gorkom, as the superlattice compounds Ga₂O₃(ZnO)_k were not clearly reported at that time. Also of importance is that these Raman peaks in our samples are much broader than those reported by Van Gorkom *et al.*²³; this is similar to what we have observed in the Raman spectra of In₂O₃(ZnO)_k superlattices²⁵.

Furthermore, in combination with X-ray diffraction results, only the Raman peak at 611 cm⁻¹ may be undoubtedly recognized as the T_{2g} mode of ZnGa₂O₄ spinel phase. As both 4 and 18 mol. % GaO_{1.5} doped ZnO are found to have Ga₂O₃(ZnO)₉ superlattice structures by X-ray diffraction analysis, together with the HRTEM observations of the nanostructures, it therefore further increases the possibility that the two broad peaks centered at 577 and 636 cm⁻¹ could be characteristic Raman modes of these superlattice nanostructures instead of ZnGa₂O₄ spinel phase. These two Raman peaks, with much reduced Raman intensity, are also observed in the 2 mol. % GaO_{1.5} doped ZnO sample. With literature findings on the HRTEM observations of nanotwin boundaries in a 2 mol. % GaO_{1.5} doped ZnO¹³, as well as the X-ray (103) peak broadening we observed in this sample, it is mostly likely that nanostructures are also present in the 2 mol. % GaO_{1.5} doped ZnO. The peak information on 577 cm⁻¹ Raman mode observed for these Ga doped ZnO were summarized in Table 1, including the calibrated peak position, relative peak

intensity and the width. It can be seen that with increasing Ga_{1.5} addition, the 577 cm⁻¹ Raman mode slightly moves toward large Raman shift wavenumbers. However, the most striking feature is increasing broadening and intensity of this peak with Ga_{1.5} addition, which implies an increasing fraction of Ga₂O₃(ZnO)_k superlattice nanostructures. In addition, a systematic shift and broadening of ZnO Raman modes with increasing Ga addition, such as E₂ mode at 101 and 438 cm⁻¹, was also observed, which also indicates an increasing portion of strained or defective lattice.

Table 1: Summaries of information on 577 cm⁻¹ Raman peak.

mol. % GaO _{1.5}	Calibrated peak position, cm ⁻¹	Relative intensity, %	Width, cm ⁻¹
2	577.17	8.56	22.02122
4	577.41	18.21	28.26039
18	577.64	29.80	31.76983

These findings suggest that the Ga solubility in ZnO is around 2 mol. %, similar to the findings by Wang *et al.*⁸ who reports a 2.7 mol. % Ga solubility in ZnO in the temperature range of 1000 to 1200 °C. Exceeding the Ga solubility in ZnO phase may result in one or both of the following consequences: the formation of ZnGa₂O₄ spinel phase as similar to the Al doped ZnO system^{1, 3, 26, 27, 28}, and/or the homologous Ga₂O₃(ZnO)_k superlattice compounds which have been reported in literatures^{11, 12, 13, 15}, as similar to the indium doped ZnO system^{19, 29, 30, 31}. Our XRD, Raman and HRTEM

observations, together with literature reports, suggest that the $\text{Ga}_2\text{O}_3(\text{ZnO})_k$ superlattice compounds are already formed in the 2 mol. % $\text{GaO}_{1.5}$ sample whereas a detectable fraction of ZnGa_2O_4 spinel phase forms in the 18 mol. % $\text{GaO}_{1.5}$.

Thermal Transport Properties

Based on Wiedemann-Franz law, the electronic contribution to the thermal conductivity κ_{el} is given by

$$\kappa_{el} = L\sigma T \quad (2)$$

where L is Lorentz factor having a typical value of $2.4 \times 10^{-8} \text{ J}^2\text{K}^{-2}\text{C}^{-2}$ for free electrons, σ is electrical conductivity and T is the absolute temperature. However, as shown in Figure 5, electrical conductivities of all the samples across the measurement temperatures are not high enough to consider the electronic contribution to the thermal conductivity. For instance, taking the highest electrical conductivity of $\sim 10 \text{ S/cm}$, we found $\kappa_{el} \approx 2.6 \times 10^{-2} \text{ W/mK}$ which is orders of magnitude smaller than the measured total thermal conductivity. Accordingly, only lattice or phonon thermal conductivity will be considered in the following discussions.

Drastic reduction of thermal conductivity with Ga addition was observed suggesting the enhanced phonon scatterings due to the introduction of defects. In addition, the significantly reduced temperature dependence of thermal conductivity with Ga addition implies the switching of dominant phonon scattering from phonon – phonon interactions, which is temperature dependent, towards a combination of point defect and interface scatterings. Although, the ZnGa_2O_4 spinel phase was present in 18 mol. %

GaO_{1.5} doped ZnO, it has a minor phase fraction (at most ~ 0.20 in the 18 mol. % GaO_{1.5} sample) and an average grain size of about 1 μm found by our electron microscopy observations. This suggests that the role of ZnGa₂O₄ spinel phase on affecting phonon transport is much less critical as compared to the Ga-doping introduced point defects and superlattice / nanotwin interfaces that have much smaller length scale.

Using the Debye model, the general expression for thermal conductivity is the integration over the entire phonon frequency spectrum which can be further written in terms of specific heat $C(\omega)$, sound velocity v_s and phonon mean free path $l(\omega)$,

$$\kappa = \int \kappa(\omega) d\omega = \frac{1}{3} \int C(\omega) v_s l(\omega) d\omega \quad (3)$$

For the point defect scattering effect, the thermal conductivity κ is inversely proportional to the square root of the point defect phonon scattering factor Γ ,

$$\kappa \propto \Gamma^{-\frac{1}{2}} \quad (4)$$

where Γ is defined as,

$$\Gamma = \sum_i f_i \left(1 - \frac{M_i}{M}\right)^2 \quad (5)$$

where M_i is the mass of a unit cell and f_i is the fraction of the unit cells with mass M_i , and M is the average mass of all cells. As seen from equation 5, the point defect scattering strength parameter depends on both defect type and concentration. Doping gallium into ZnO creates gallium substitutional ions on zinc sites as well as zinc vacancies for charge compensation while there are no defects on anion sites³². The corresponding defect reaction is given by,

and the chemical formula of gallium doped ZnO is

$$\left(\text{Zn}_{1-\frac{3}{2}c} \text{Ga}_c \text{V}_{\frac{c}{2}} \right) \text{O} \quad (7)$$

where c is the gallium concentration in ZnO lattice. Taking into account both the substitutional gallium ions on zinc site and zinc vacancy, the point defect scattering strength parameter can be written as,

$$\Gamma = c \frac{(M_{\text{Ga}} - \overline{M}_{\text{Zn}})^2}{2(\overline{M}_{\text{ZnO}})^2} + \frac{c}{2} \frac{(\overline{M}_{\text{Zn}})^2}{(\overline{M}_{\text{ZnO}})^2} \quad (8)$$

where $\overline{M}_{\text{ZnO}}$ is the mean mass of the doped ZnO formula unit and $\overline{M}_{\text{Zn}}$ is the average atomic mass on zinc site, both of which are dependent on gallium concentration c in ZnO lattice.

Superlattice interfaces or nanotwin boundaries, as striking features of Ga doped ZnO, also play a very important role in reducing the thermal conductivity, as clearly seen from equation 4 that thermal conductivity decreases with reducing phonon mean free path l . The lower bound for the average $\text{Ga}_2\text{O}_3(\text{ZnO})_k$ superlattice interface spacing L can be estimated based on the chemical composition and a value of $L \sim 26$ nm was found for the 2 mol. % $\text{GaO}_{1.5}$ doped ZnO. Our microscopy reveals that the average nanotwin boundary spacing is about ~ 3 nm, while the interfacial spacing of Ga-O layers in the $\text{Ga}_2\text{O}_3(\text{ZnO})_9$ superlattice phase is even smaller and is about $\frac{c_0}{2} \approx 1.65$ nm where c_0 is the unit cell parameter of $\text{Ga}_2\text{O}_3(\text{ZnO})_9$ modular compound^{11, 12}. With the interface spacing reducing from ~ 26 to 1.65 nm, the room temperature thermal conductivity decreases from

11.6 to 3.1 W/mK, which is about a four-fold reduction, demonstrating the nanostructure interface engineering as an effective approach to further lower the thermal conductivity.

Electrical Transport Properties

All the Ga doped ZnO samples demonstrate larger electrical conductivity as compared to the undoped ZnO, as shown in Figure 5. This suggests that the doped Ga ions provide the electron donors and therefore increase the charge carrier concentration. However, through the entire measurement temperature, the electrical conductivity basically decreases with the increasing Ga addition, with 18 mol. % Ga_{1.5} doped ZnO having the lowest electrical conductivity. The systematic decrease of electrical conductivity with Ga addition can be correlated with the change in phase compositions and structure. As has been discussed previously, based on various characterization techniques, there is no doubt that ZnGa₂O₄ spinel phase formed in the 18 mol. % Ga_{1.5} doped ZnO. This spinel phase is a less electrical conducting phase than pure ZnO, due to its large band gap of 4.0 eV and electrical conductivity of 10⁻¹ S/cm at 290 K ³³ as compared with the band gap of 3.3 eV for ZnO ³⁴. This is very similar to the observations on Al doped ZnO where electrical conductivity initially increases with Al addition but drops when the Al solubility in ZnO lattice is reached and a less conducting ZnAl₂O₄ spinel phase forms ². Furthermore, the content of superlattice or nanotwin interfaces increases with Ga addition; these nanostructures can also scatter electrons to some extent and induce an increase in electrical resistivity ¹⁵.

The superlattices are essentially interfaces of single-atomic sheets, while the nanotwins are grain boundaries. These nanoscale interfaces are basically two-dimensional or planar defects in a single-phase matrix, being obstacles for affecting electron and phonon transfer. One may also consider treating the materials as multi-phase system, the finite element method (FEM) modeling or effective medium theory, for instance, could be approaches to be used. However, the challenge then rises up that the intrinsic properties of the superlattices are mostly unavailable, since the ordered natural superlattices are usually difficult to obtain. Furthermore, the effect of the interfaces is usually not considered in these approaches^{35, 36}. The difference between these analyzing approaches is, to some extent, the length scale that we are considering. In the present work, we consider the electron transport from the microscopic scale and treat the superlattices and nanotwins as planar defects in the matrix. Whereas the 18 mol. % GaO_{1.5} doped ZnO contains a detectable fraction of ZnGa₂O₄ spinel phase, and therefore is no longer a single-phase. While in this work, we believe that the effect of the ZnGa₂O₄ phase is relatively negligible, as can be seen as follows. First, it has a small fraction. Second, and also more importantly, the typical grain size of ZnGa₂O₄ spinel phase, which is a few micrometers, is far larger than the spacing of the superlattices and nanotwins that are a few nanometers, and therefore much less significant than the latter (the nanoscale interfaces) in affecting the thermoelectric transport, considering the electron and phonon mean free path. Accordingly, in the following content we shall analyze and discuss the thermoelectric transport properties by treating the materials as a single-phase system that consists of point and nanoscale planar defects.

All the Ga doped ZnO samples investigated in the present work demonstrate an increase of both electrical conductivity and Seebeck coefficient with temperature, especially the 2 mol. % Ga_{1.5} doped ZnO. This finding is opposite to the commonly observed non-degenerate semiconductor behavior such as the undoped ZnO, in which electrical conductivity increases whereas Seebeck coefficient decreases with temperature, as the two parameters have opposite dependence on temperature ³⁷. Temperature dependence of Seebeck coefficient of a semiconducting material is normally related to its band gap E_g as follows ³⁸,

$$S \approx \left(\frac{k_B}{e}\right) \frac{E_g}{k_B T} \quad (9)$$

where k_B is the Boltzmann's constant and e is the electronic charge. Our observations that the Seebeck coefficient of Ga doped ZnO materials does not follow the temperature dependence given by equation 9 suggest that the Ga doped ZnO in the current work may no longer be non-degenerate. In the following content, we shall apply a physical model based on Seebeck coefficient to confirm this is indeed the case.

Seebeck coefficient is sensitive to the change of Fermi level and has been used to investigate the electron conduction process in semiconductor materials ^{39, 40, 41, 42, 43}. Fritzsche ⁴⁴ derived a model in which the correlation between Seebeck coefficient and Fermi level is clearly presented. For the n-type semiconductor, one has

$$S = -\frac{k_B}{e} \left[\frac{E_C - E_F}{k_B T} + A_C \right] \quad (10)$$

where E_C and E_F are conduction band edge and Fermi level, respectively. The term A_C is given by,

$$A_C = \frac{\int_0^\infty \frac{E - E_C}{k_B T} \sigma(E) dE}{\int_0^\infty \sigma(E) dE} \quad (11)$$

which is a temperature independent constant, accounting for the carriers that are distributed beyond the conduction band E_C .

It should be noted that the bandgap E_g , the conduction band edge E_C and the Fermi level E_F are all dependent on temperature. The change of conduction band edge E_C with temperature associated with the bandgap E_g change can be well approximated by a linear relationship ⁴⁵, according to which the term E_C in equation 10 is replaced by $(E_C + \gamma_g T)$ where γ_g is a temperature dependent density of states gap coefficient. Similarly, the shift of Fermi level E_F with respect to temperature can be given by $(E_F + \gamma_F T)$ ^{40, 42} where γ_F is also a temperature coefficient. In fact, the temperature dependence of Fermi level becomes drastically weak as doping or carrier concentration increases ⁴⁶. Accordingly, equation 10 can be written as,

$$-S = \frac{E_C - E_F}{e} \left(\frac{1}{T} \right) + \left[\frac{\gamma_g - \gamma_F}{e} + A_C \frac{k_B}{e} \right] \quad (12)$$

The above equation suggests a linear dependence of $-S$ with $1/T$ and the slope gives the Fermi level measured from the conduction band edge. In Figure 7, the negative Seebeck coefficient $-S$ is plotted against the inverse of absolute temperature $1/T$. The measured data are shown by the scattered symbols while the modeling fit of the data according to equation 12 are represented by the dashed lines. Generally most of the data were reasonably well fit into the model. The derived Fermi levels as measured from the conduction band edge, $E_C - E_F$, are also indicated on the figure. We found the value of $E_C - E_F$ is + 0.066 eV for ZnO, - 0.049 eV for 2 mol. %, - 0.106 eV for 4 mol. % and -

0.102 eV for 18 mol. % GaO_{1.5} doped ZnO, respectively. This suggests that the Fermi level shift above the conduction band edge in all the Ga doped ZnO samples investigated in the current work and the materials become degenerate, which are consistent with literature findings by photoelectron spectroscopy and band structure calculations ⁴⁷. The Fermi level found for ZnO seems to be too close to the conduction band for an undoped material. However, it has been commonly found that the native defects in ZnO such as oxygen vacancies can significantly affect the Fermi level and electronic transport properties ^{48, 49}. While with these materials degenerate, relatively positive temperature dependence of electrical conductivity is observed for all these GaO_{1.5} doped samples, as different from the ordinary metallic oxide semiconductors. All the very small doping bandwidth ($E_F - E_C \approx 0.5 \sim 1.0$ eV) is the major reason. Both excitation of deeper electronic defects and ionization of impurities increases with temperature. The former one increases the carrier concentration and the latter makes the temperature dependence of mobility tend to be positive, both of which contribute to the positive temperature dependence of electrical conductivity.

Figure 7: Plot of negative Seebeck coefficient $-S$ against the inverse of absolute temperature $1/T$. Experimental data are shown as scattered symbols and modeling fit according to equation 12 are represented by dashed lines. The derived Fermi levels estimated for each sample, as measured from conduction band edge, $E_C - E_F$, are indicated besides each set of data.

With the finding that the Ga doped ZnO in the current work are degenerate semiconductors, it is valid to adopt the Seebeck model for metallic or degenerate semiconductors. By combining it with the electrical conductivity measurements, we are able to illuminate the dominant electron scattering mechanisms in these samples. For metallic or degenerate semiconductors, the Seebeck coefficient is given by the following relation^{37,38},

$$S \approx \frac{2k_B^2}{e\hbar} m^* T (3\pi^2 n)^{-\frac{2}{3}} \quad (13)$$

where n is the carrier concentration and m^* is the effective mass of charge carriers. The above equation suggests that the Seebeck coefficient is mostly controlled by the change in temperature and carrier concentration, i.e.

$$S \propto T \cdot n(T)^{-\frac{2}{3}} \quad (14)$$

It is noted that the carrier concentration $n(T)$ is also dependent on temperature T , which can be extracted from the temperature dependence of electrical conductivity $\sigma(T)$, according to the following equation,

$$\sigma(T) = n(T)e\mu(T) \quad (15)$$

where $\mu(T)$ is the electron mobility and is also a function of temperature⁵⁰,

$$\mu(T) = \frac{4}{3\pi^{\frac{1}{2}}} \Gamma\left(r + \frac{5}{2}\right) \frac{e\tau_0(k_B T)^r}{m^*} \quad (16)$$

in which Γ here is the gamma function, $\tau_0(k_B T)^r = \tau_e$ is the electron relaxation time where τ_0 and r are constants for a given scattering process. The important constant in this equation is r which reflects the temperature dependence of carrier mobility. The two bounds or extreme values of r are $-3/2$ for electron scattering dominated by lattice vibrations or phonons, and $3/2$ for ionized impurities dominated scattering, respectively. In compilation of the equations 13 to 16 with experimental data of electrical conductivity, the temperature dependence of Seebeck coefficient can be modelled with r as the only fitting parameter. As shown in Figure 6, the best modeling fit of the temperature dependence of Seebeck coefficient for all the Ga doped ZnO are represented by dashed lines. The model describes reasonably well the temperature dependence of Seebeck coefficients measured in all the Ga doped ZnO. Since both lattice phonons and impurities

are present, the derived value of r is a reflection of a combination of the two electron scattering mechanisms. The dominant mechanism can be indicated based on its sign and value.

Lattice (phonon) scattering, which mostly dominates in the undoped or lightly doped materials, is found to be the primary electron scattering mechanism in the 2 mol. % GaO_{1.5} doped ZnO for which a negative value of $r = -0.1$ was obtained. This suggests that electron mobility decreases with temperature, as at higher temperatures there are more phonons and therefore increased phonon scatterings that reduce the electron mobility. On the other hand, ionized impurity scattering is normally observed in the heavily doped materials and found to be governing in the 4 and 18 mol. % GaO_{1.5} samples, both of which have a derived r value of 0.32. When ionized impurities are the main source of scattering, electron mobility increases with temperature as the thermal speeds of the carriers increase with temperature and therefore spends less time near an ionized impurity, leading to a reduced ion impurity scattering effect. The above combined analysis of electrical conductivity and Seebeck coefficient with temperature suggests a transition in the dominant electron scattering mechanism with Ga addition, i.e. from lattice or phonon scattering to ionized impurity scattering. Apparently taking the derived values of r back to the equation 16, the 2 mol. % GaO_{1.5} sample has a negative temperature dependence of electron mobility while 4 and 18 mol. % samples have positive temperature dependence, since the dominant electron scattering mechanism switches from the lattice vibration to the impurity or defect scattering mode. From this sense, the heavily doped sample should demonstrate more positive temperature dependence of electrical conductivity. However, the measured electrical conductivity

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4 data against temperature, as shown in Figure 5, is not exactly like this. The electrical
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6 conductivity of 4 and 18 mol. % $\text{GaO}_{1.5}$ doped samples is relatively invariant with
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8 temperature; this is characteristic of electron tunneling. This is attributed to the presence
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10 of $\text{Ga}_2\text{O}_3(\text{ZnO})_k$ superlattices in the 4 and 18 m/o Ga doped samples, which consists of
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12 Ga-O single atomic layers. Due to these high density nanoscale interfaces, electron
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14 tunneling becomes significant and takes a role in the electron transport behavior.
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20 Based on the measured thermal conductivity, electrical conductivity and Seebeck
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22 coefficient, the figure of merit ZT is readily obtained, as presented in Figure 8.
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24 Apparently, the Ga-ZnO ceramics have demonstrated much improved thermoelectric
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26 performance over the pure ZnO, and show compatible thermoelectric properties with
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28 other ZnO based binary oxide thermoelectrics, like Fe-ZnO, Ni-ZnO and In-ZnO
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30 ceramics whose literature reported ZT values are also shown in Figure 8. The
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32 thermoelectric properties of Ga-ZnO ceramics still lag far behind the metallic or
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34 semiconductor thermoelectric materials, while with the drastically reduced thermal
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36 conductivity due to the ability of forming natural nanostructures, efforts are oriented to be
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38 made on improving the electrical properties, for instance, by dual doping, to make the
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40 Ga-ZnO ceramics potential for high temperature thermoelectric application.
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Figure 8: Figure of merit for the Ga-ZnO ceramics with temperature. The literature reported data of single element doped ZnO are also presented for comparison, including Fe-ZnO^{25, 51}, Ni-ZnO⁵² and In-ZnO^{25, 53} ceramics. The lines through the data points are the least square fit for the vision guide.

Conclusions

In conclusion, high temperature thermoelectric properties and compositionally dependent structures of Ga-ZnO ceramics are investigated. At low Ga addition, a ZnO solid solution phase is present with point defects and fine structures, which reduces thermal conductivity. Electrical conductivity was significantly improved due to the increased carrier concentration. With further increasing Ga addition beyond the solubility limit in ZnO lattices, a $\text{Ga}_2\text{O}_3(\text{ZnO})_9$ homologous superlattice structure with nanotwins as well as ZnGa_2O_4 spinel phase are formed, both of which are less electrically conductive. The thermal conductivity, due to the additional phonon scattering by nanostructure

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4 interfaces, is substantially lowered in almost four-fold reduction. Analysis of the
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6 temperature dependent Seebeck measurement suggests Ga doping moves the Fermi level
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8 above the conduction band and the materials become degenerate. A combined analysis of
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10 electrical conductivity and Seebeck coefficient with temperature is developed and applied
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12 to the measured data, which reveals the change of the dominant electron scattering
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14 mechanism with Ga addition. The capability of tuning electrical properties and achieving
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16 low thermal conductivity with natural nanostructures makes the Ga-ZnO ceramics
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18 potential for high temperature thermoelectric applications.
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48 **Additional Information:**

51 The author declares no competing financial interests.
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- 19) and $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ ($m = 8$ and 9) in the $\text{In}_2\text{O}_3\text{-ZnFe}_2\text{O}_4\text{-ZnO}$ system. *Journal of Solid State Chemistry* **103**, 394-402 (1993).
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Table

Table 1: Summaries of information on 577 cm⁻¹ Raman peak.

mol. % GaO _{1.5}	Calibrated peak position, cm ⁻¹	Relative intensity, %	Width, cm ⁻¹
2	577.17	8.56	22.02122
4	577.41	18.21	28.26039
18	577.64	29.80	31.76983

Figure captions:

Figure 1: X-ray diffraction data of Ga doped ZnO after 1150 °C 1 day thermal treatment.

The characteristic peaks of $\text{Ga}_2\text{O}_3(\text{ZnO})_9$, ZnGa_2O_4 spinel and ZnO phases are shown at the bottom of the figure. A few of most distinguishable ZnGa_2O_4 spinel peaks are also indicated by the vertical dashed red lines.

Figure 2: Raman spectra of Ga doped ZnO annealed at 1150 °C for 1 day; pure ZnO data was also enclosed. The characteristic Raman modes for ZnO and ZnGa_2O_4 spinel phase are indicated by olive and red colored labels, respectively. Raman modes of interests in the present work are also indicated by the dashed lines across all the spectra.

Figure 3: HRTEM image (a) and the corresponding diffraction pattern (b) of superlattice structures with nanotwins in 18 mol. % $\text{GaO}_{1.5}$ doped ZnO. The HRTEM image reveals the nanotwin boundary with a crystallographic angel of about 60 °. The electron diffraction pattern was taken along the $[\bar{1}2\bar{1}0]$ direction, which consists of two sets of lattices; in addition, diffuse superlattice reflection streaks were also observed.

Figure 4: Thermal conductivity measured with temperature for Ga doped ZnO samples with data of undoped ZnO shown for comparisons, represented by scattered symbols. All the samples presented on this figure were annealed at 1150 °C for 1 day. The lines through the data points are the least square fit.

Figure 5: Electrical conductivity of Ga doped ZnO measured with temperature up to 800 °C. Pure ZnO data are also indicated. The lines through the data points are the least square fit.

Figure 6: Seebeck coefficient of Ga doped ZnO measured with temperature up to 800 °C. The experiment results are shown as scattered symbols, and the modeling fits of the measured data are represented by dashed lines with the same colors of the measurement data symbols.

Figure 7: Plot of negative Seebeck coefficient $-S$ against the inverse of absolute temperature $1/T$. Experimental data are shown as scattered symbols and modeling fit according to equation 12 are represented by dashed lines. The derived Fermi levels estimated for each sample, as measured from conduction band edge, $E_C - E_F$, are indicated besides each set of data.

Figure 8: Figure of merit for the Ga-ZnO ceramics with temperature. The literature reported data of single element doped ZnO are also presented for comparison, including Fe-ZnO^{25,51}, Ni-ZnO⁵² and In-ZnO^{25,53} ceramics. The lines through the data points are the least square fit for the vision guide.