Effects of morphology on the thermoelectric properties of Al-doped ZnO – Supplementary information

Li Han,a Ngo Van Nong,a Wei Zhang,a Le Thanh Hung,a Tim Holgate,a Kazunari Tashiro,b Michitaka Ohtaki,b Nini Pryds,a* and Søren Linderotha

a Department of Energy Conversion and Storage, Technical University of Denmark, DTU Risø Campus, Frederiksborgvej 399, 4000 Roskilde, Denmark.

b Department of Molecular and Materials Sciences, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasugakoen, Kasuga, Fukuoka 816-8580, Japan

Table of Contents:
1. Powder X-ray diffraction pattern of the precursors
2. STEM-EDS mapping of the nanonuclei
3. SEM-EDS analysis of the fractured surface of bulk samples
4. Thermal diffusivity data
5. Specific heat at constant pressure data
6. Calculations of The lower limit of thermal conductivity \( \kappa_{\text{min}} \)
7. Calculations of The lattice thermal conductivity \( \kappa_L \)

* To whom correspondence should be addressed. E-mail: nipr@dtu.dk
Figure S1. The powder X-ray diffraction pattern of the precursors with different morphologies.

Figure S2. STEM-EDS mapping of the nanoparticles synthesized by forced-hydrolysis method.
Figure S3. EDS point analysis of the secondary phases dispersed on the fractured surface of (a) Platelet(\(\perp\)p) surface, (b) Platelet(\(\parallel\)p) surface, (c) Rod(\(\perp\)p) surface, (d) Rod(\(\parallel\)p) surface, and (e) Nanoparticle.

Figure S4. Temperature dependence of thermal diffusivity of the sintered samples measured by LFA.
**Calculations of The lower limit of thermal conductivity $\kappa_{\text{min}}$**

The lower limit of thermal conductivity $\kappa_{\text{min}}$ for Zn$_{0.98}$Al$_{0.02}$O was calculated by taking the high-temperature limit of the thermal conductivity calculated by Cahill et al$^1$ for amorphous material with an average volume per atom given by $V$.

$$\kappa_{\text{min}} = \frac{1}{2} \left( \frac{\pi}{6} \right)^{\frac{1}{3}} k_B \left[ \frac{2}{(2 v_t + v_l)} \right]$$

where $k_B$ is Boltzmann constant, $v_t$ and $v_l$ are transverse and longitudinal speed of sound. From the speed of sound measurements, $v_t$ here equals 2750 m·s$^{-1}$, and $v_l$ equals 5940 m·s$^{-1}$. Thus the $\kappa_{\text{min}}$ was calculated to be 1.22 W·m$^{-1}$·K$^{-1}$ as shown in Figure 8 in the main article.

**Calculations of The lattice thermal conductivity $\kappa_L$**

The lattice thermal conductivity is calculated using Debye-Callaway model$^{2,3}$ as follows:

$$\kappa_L = \frac{k_B}{2\pi^4 \nu} \left( \frac{\hbar}{\hbar} \right)^{3} \left[ \int_0^{\frac{1}{k_B T}} r_c x^4 e^{-x} \frac{dX}{(e^x - 1)^2} + \int_0^{\frac{1}{k_B T}} r_c x^4 e^{-x} \frac{dX}{(e^x - 1)^2} \right]$$

where $k_B$ is Boltzmann constant, $\nu$ is the speed of sound, $\hbar$ is reduced Planck’s constant, $x$ is the normalized frequency $\hbar\omega/k_B T$, $T$ is the absolute temperature, $\theta$ is the Debye temperature of Zn$_{0.98}$Al$_{0.02}$O. $\tau_c$ is the combine relaxation time using Matthiessen’s rule as follows:

$$\tau_c^{-1} = \tau_{pd}^{-1} + \tau_N^{-1} + \tau_B^{-1} + \tau_D^{-1}$$

(3)
where \( \tau_c \) is composed of point defect scattering \( \tau_{pd} \), normal phonon-phonon scattering \( \tau_N \), boundary scattering \( \tau_B \), and nano-particle scattering \( \tau_D \). The relaxation time for these scattering mechanisms is calculated from the following relations:

\[
\tau_{pd}^{-1} = A \omega^4 = a T^4 x^4 \quad (4)
\]

\[
\tau_N^{-1} = BT^3 \omega^2 = \beta T^5 x^2 \quad (5)
\]

\[
\tau_B^{-1} = \nu/L \quad (6)
\]

where \( A, B, \alpha \) and \( \beta \) are scattering strength related parameters, \( \omega \) is phonon frequency, \( L \) is the average grain size values. According to Majumdar’s heat transfer theory,\(^4,5\) when the particle size is small enough, the scattering cross section obeys Rayleigh law, which varies as frequency to the fourth power. Thus the relaxation time for nanonuclei scattering, \( \tau_D \), should be calculated as:

\[
\tau_D^{-1} = \eta v^{-3} (2\pi)^{-4} d^6 \omega^4 = (2\pi)^{-4} \eta v^{-3} d^6 k_B T^4 \hbar^{-4} x^4 \quad (7)
\]

where \( \eta \) is concentration \((\text{m}^{-3})\). \( d \) is the mean nano-particle size. As the size of nano-particle increases, the scattering cross section is near geometric and phonon frequency independent, which is \( \sigma_{\text{(geometric)}} \sim \pi(d/2)^2 \). Thus the relaxation time for nanonuclei scattering, \( \tau_D \), should be calculated as:

\[
\tau_D^{-1} = \eta v \pi (d/2)^2 \quad (8)
\]

The values used for the calculations are listed in the following Table S1.

**Table S1**

An overview of the parameters used in Callaway calculations

<table>
<thead>
<tr>
<th>Calculation</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
<th>#4</th>
<th>#5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>Rod (⊥p)</td>
<td>Rod (∥p)</td>
<td>Plate (⊥p)</td>
<td>Plate (∥p)</td>
<td>Nano</td>
</tr>
<tr>
<td>0/K</td>
<td>400</td>
<td>400</td>
<td>400</td>
<td>400</td>
<td>400</td>
</tr>
<tr>
<td>( v/\text{ms}^{-1} )</td>
<td>3097</td>
<td>3097</td>
<td>3097</td>
<td>3097</td>
<td>3097</td>
</tr>
<tr>
<td>( \alpha/\text{K}^{-4}\text{s}^{-1} )</td>
<td>420</td>
<td>420</td>
<td>400</td>
<td>400</td>
<td>100</td>
</tr>
<tr>
<td>( \beta/\text{K}^{-5}\text{s}^{-1} )</td>
<td>0.015</td>
<td>0.015</td>
<td>0.015</td>
<td>0.015</td>
<td>0.015</td>
</tr>
<tr>
<td>L/m</td>
<td>( 1 \times 10^{-5} )</td>
<td>( 2 \times 10^{-6} )</td>
<td>( 6 \times 10^{-7} )</td>
<td>( 1.5 \times 10^{-7} )</td>
<td>( 4 \times 10^{-7} )</td>
</tr>
<tr>
<td>( \eta_{\text{(geometric)}}/\text{m}^{-3} )</td>
<td>( 1.2 \times 10^{17} )</td>
<td>( 1.2 \times 10^{17} )</td>
<td>( 1 \times 10^{19} )</td>
<td>( 1 \times 10^{19} )</td>
<td></td>
</tr>
<tr>
<td>( d_{\text{(geometric)}}/\text{m} )</td>
<td>( 3 \times 10^{-7} )</td>
<td>( 3 \times 10^{-7} )</td>
<td>( 3 \times 10^{-8} )</td>
<td>( 3 \times 10^{-8} )</td>
<td></td>
</tr>
<tr>
<td>( \eta_{\text{(Rayleigh)}}/\text{m}^{-3} )</td>
<td>1.4 ( \times 10^{20} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( d_{\text{(Rayleigh)}}/\text{m} )</td>
<td>1 ( \times 10^{-8} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


