Electronic Supplementary Material (ESI) for RSC Advances.

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

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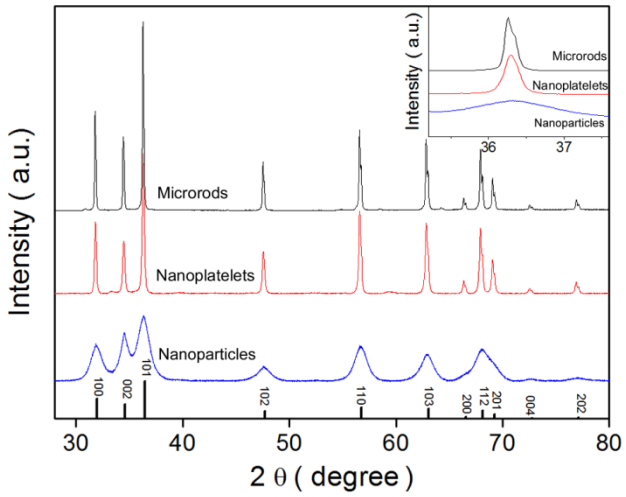

Figure S1. The powder X-ray diffraction pattern of the precursors with different morphologies.

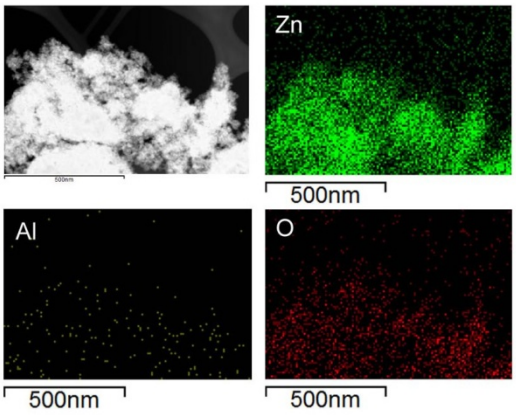

Figure S2. STEM-EDS mapping of the nanoparticles synthesized by forced-hydrolysis method.

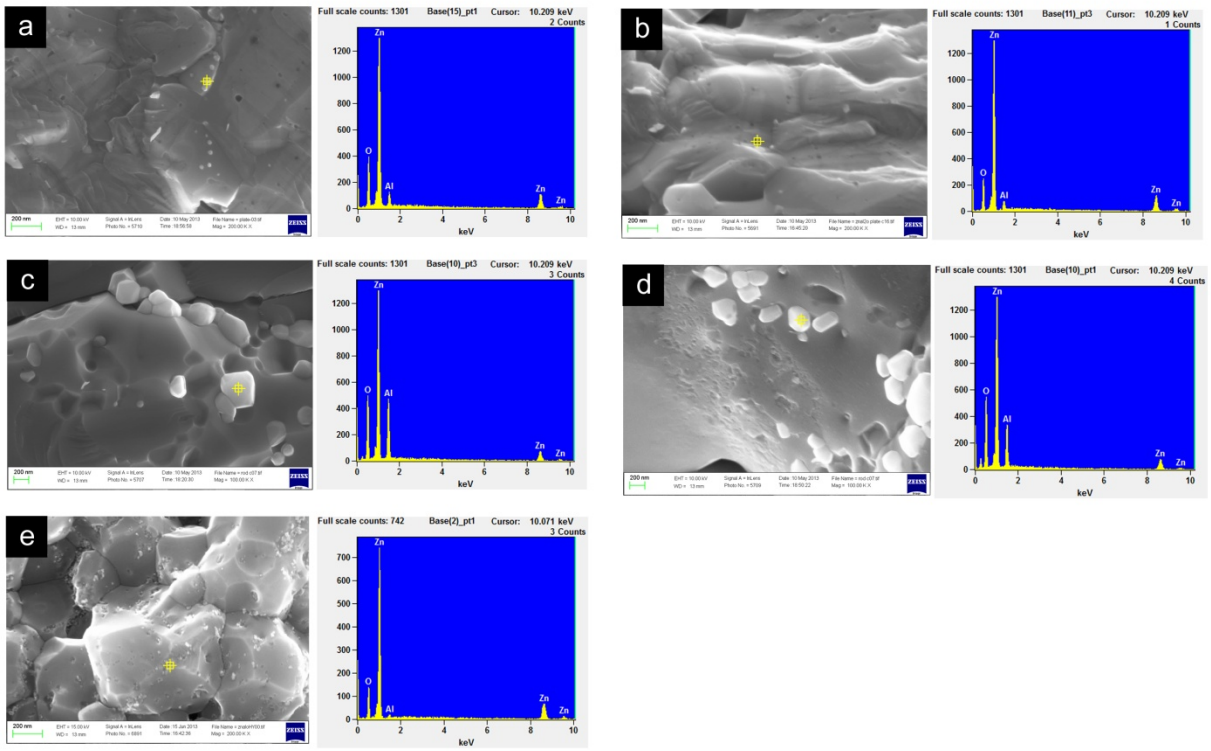

Figure S3. EDS point analysis of the secondary phases dispersed on the fractured surface of (a) Platelet(⊥p) surface, (b) Platelet(‖ p) surface, (c) Rod(⊥p) surface, (d) Rod(‖ p) surface, and (e) Nanoparticle.

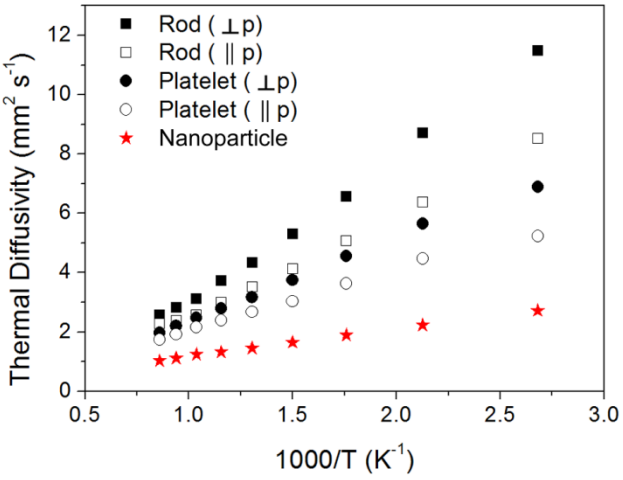

Figure S4. Temperature dependence of thermal diffusivity of the sintered samples measured by LFA.

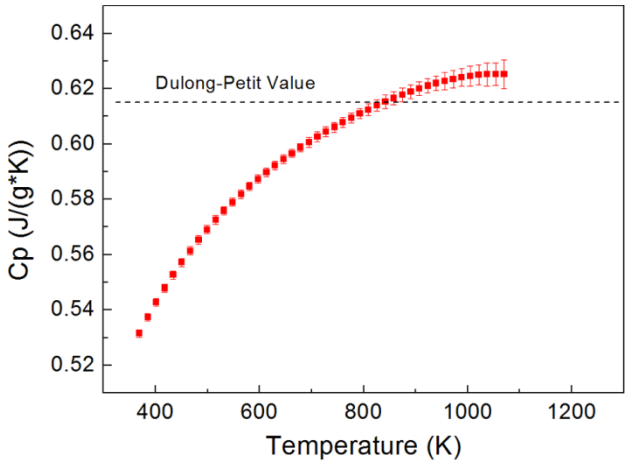

Figure S5. Temperature denpendence of the specific heat at constant pressure measured by DSC.

Calculations of The lower limit of thermal conductivity κ_{min}

The lower limit of thermal conductivity κ_{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.

$$\kappa_{min} = \frac{1}{2}\left(\frac{\pi}{6}\right)^{\frac{1}{3}} k_B V^{-\frac{2}{3}} (2v_t + v_l) \quad (1)$$

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 $m \cdot s^{-1}$, and v_l equals 5940 $m \cdot s^{-1}$. Thus the κ_{min} was calculated to be 1.22 $W \cdot m^{-1} \cdot K^{-1}$ as shown in Figure 8 in the main article.

Calculations of The lattice thermal conductivity κ_L

The lattice thermal conductivity is calculated using Debye-Callaway model[2,3] as follows:

$$\kappa_L = \frac{k_B}{2\pi^2 v}\left(\frac{k_B T}{\hbar}\right)^3 \left\{ \int_0^{\theta/T} \frac{\tau_c x^4 e^x}{(e^x-1)^2} dx + \frac{\left[\int_0^{\theta/T} \frac{\tau_c}{\tau_N} \frac{x^4 e^x}{(e^x-1)^2} dx\right]^2}{\int_0^{\theta/T} \frac{1}{\tau_N}\left(1-\frac{\tau_C}{\tau_N}\right) \frac{\tau_c x^4 e^x}{(e^x-1)^2} dx} \right\} \quad (2)$$

where k_B is Boltzmann constant, v 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, θ is the Debye temperature of $Zn_{0.98}Al_{0.02}O$. τ_c is the combine relaxation time using Matthiessen's rule as follows:

$$\tau_c^{-1} = \tau_{pd}^{-1} + \tau_N^{-1} + \tau_B^{-1} + \tau_D^{-1} \quad (3)$$

where τ_c is composed of point defect scattering τ_{pd}, normal phonon-phonon scattering τ_N, boundary scattering τ_B, and nano-particle scattering τ_D. The relaxation time for these scattering mechanisms is calculated from the following relations:

$$\tau_{pd}^{-1} = A\omega^4 = \alpha T^4 x^4 \quad (4)$$

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

$$\tau_B^{-1} = v/L \quad (6)$$

where *A, B,* α and β are scattering strength related parameters, ω 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, τ_D, should be calculated as:

$$\tau_{D(Rayleigh)}^{-1} = \eta\, v^{-3}\,(2\pi)^{-4} d^6 w^4 = (2\pi)^{-4}\eta\, v^{-3}\, d^6 k_B^4 T^4 \hbar^{-4} x^4 \quad (7)$$

where η is concentration (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 $\sigma_{(geometric)} \sim \pi(d/2)^2$. Thus the relaxation time for nanonuclei scattering, τ_D, should be calculated as:

$$\tau_{D(geometric)}^{-1} = \eta\, v\, \pi(d/2)^2 \quad (8)$$

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

Table S1

An overview of the parameters used in Callaway calculations

Calculation	#1	#2	#3	#4	#5
Sample	Rod (⊥p)	Rod (‖p)	Plate (⊥p)	Plate (‖p)	Nano
θ/K	400	400	400	400	400
v/ms^{-1}	3097	3097	3097	3097	3097
α/$K^{-4}s^{-1}$	420	420	400	400	100
β/$K^{-5}s^{-1}$	0.015	0.015	0.015	0.015	0.015
L/m	1×10^{-5}	2×10^{-6}	6×10^{-7}	1.5×10^{-7}	4×10^{-7}
$\eta_{(geometric)}/m^{-3}$	1.2×10^{17}	1.2×10^{17}	1×10^{19}	1×10^{19}	
$d_{(geometric)}$/m	3×10^{-7}	3×10^{-7}	3×10^{-8}	3×10^{-8}	
$\eta_{(Rayleigh)}/m^{-3}$					1.4×10^{20}
$d_{(Rayleigh)}$/m					1×10^{-8}

(1) Cahill, D. G.; Watson, S. K.; Pohl, R. O. Lower Limit to the Thermal Conductivity of Disordered Crystals. *Phys. Rev. B* **1992**, *46*, 6131.

(2) Callaway, J. Model for Lattice Thermal Conductivity at Low Temperatures. *Phys. Rev*. **1959**, *113*, 1046–1051.

(3) Dubey, K. S.; Misho, R. H. Three-phonon Scattering Relaxation Rate and Phonon Conductivity. Application to Mg2Ge. *Phys. Status Solidi B* **1977**, *84*, 69–81.

(4) Majumdar, A. Microscale Heat Conduction in Dielectric Thin Films. *J. Heat Transfer* **1993**, *115*, 7–16.

(5) Kim, W.; Majumdar, A. Phonon Scattering Cross Section of Polydispersed Spherical Nanoparticles. *J. Appl. Phys*. **2006**, *99*, 084306.