Effects of precipitation on the thermal conductivity of doped thermoelectric zinc oxide

Ido Koresh

# Effects of precipitation on the thermal conductivity of doped thermoelectric zinc oxide

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Ido Koresh

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# List of symbols

$A_m$	A defined area at SEM image
$A_p$	Precipitate average area, the surface covered by precipitates in $A_m$ divided by $n_m$ .
$C_P$	specific heat at constant-pressure
$C_v$	specific heat at constant-volume
d	An average distance between precipitates
D	Diameter of a body
$D_m$	Matrix density
f	Fractional concentration
h	Height/thickness
l	Phonon's mean free path
L	Average grain size
т	Weight (used for density calculation)
$m^*$	Effective mass
$\overline{M}$	Average atomic mass of the compound
n	Charge carrier (holes or electrons) concentration
$n_m$	The number of precipitates at a defined area at SEM images
$N_c$	Charge carrier density of state
$N_{v}$	Precipitates number density
R	Precipitate average radius
S	Seebeck coefficient - thermopower
Т	Temperature
$T_C$	Temperature at cold side
<i>t</i> <sub>0.5</sub>	Characteristic time at which the thermal signal reaches 50% of its intensity
$T_D$	Debye temperature
$T_H$	Temperature at hot side
Tref	A reference temperature
U	Umklapp processes
$V_{f}$	Volume fraction of the precipitates
ZT	Thermoelectric figure of merit

α	Thermal diffusivity
δ	Atomic volume
γ	Grüneisen parameter
Γ	Disorder parameter
η	Total efficiency of a TE module
$\mathcal{E}_i$	Phenomenological adjustable parameter
К	Thermal conductivity
Kph	Phonon contribution to thermal conductivity
Kel	Conduction electrons contribution to thermal conductivity
$\kappa_{rel}$	Relative thermal conductivity
μ	Carrier mobility
$\mathcal{U}_{S}$	Average sound velocity
ρ	Bulk density
$ ho_T$	ZnO theoretical density (5.605 g $\cdot$ cm <sup>-3</sup> )
τ	Phonon relaxation time
$ au_{GB}$	Relaxation time corresponding to grain boundaries
$ au_P$	Relaxation time corresponding to precipitates
$ au_{PD}$	Relaxation time corresponding to point defects
$ au_t$	Equivalent phonon relaxation time
$ au_U$	Relaxation time corresponding to Umklapp processes
σ	Electrical conductivity
$\sigma_{\scriptscriptstyle G}$	Effective scattering cross-section due to the Rayleigh mechanism
$\sigma_{\scriptscriptstyle R}$	Effective scattering cross-section due to near-geometrical mechanism
ω	Phonon angular frequency
$\omega_{\scriptscriptstyle D}$	Debye frequency

# List of acronyms

EBSD	Electron backscatter diffraction
EDS	Energy dispersive spectroscopy
GB	Grain boundaries - phonon scattering process
HRSEM	High-resolution scanning electron microscopy
LFA	Laser flash analysis
Р	Precipitates - phonon scattering process
PD	Solid-solution point defects - phonon scattering process
PF	Thermoelectric Power factor
%TD	Percentage of theoretical density
RT	Room temperature
SBA	Seebeck Analyser
TE	Thermoelectric
TEM	Transmission electron microscopy
XRD	X-ray Diffraction

# List of Physical Constants

e	Electron charge $1.602 \cdot 10^{-19}$ coulombs (C)
L <sub>n</sub>	Lorentz number $2.44 \cdot 10^{-8} W \cdot \Omega \cdot K^{-2}$
k <sub>B</sub>	Boltzmann constant $1.38 \times 10^{-23} J \cdot K^{-1}$
h	Planck's constant $6.626 \times 10^{-34} J \cdot s$
ħ	The reduced Planck's constant: $\hbar = h/2\pi = 1.054 \times 10^{-34} J \cdot s$

## 1. Abstract

In the thermoelectric (TE) effect thermal energy is converted into electrical energy and vice-versa, which is applicable for waste heat recovery as well as heat-exchange or refrigerating. TE performance is highly sensitive to the finest features of the microstructure, and can be tailored by manipulating material's microstructure. Zinc oxide (ZnO) is among the most promising TE materials that offer a desirable combination between reasonable conversion efficiency, chemical and structural stability at high service temperatures, as well as low cost.

In the present study we investigate the effects of precipitation on thermal conductivity of nickel-doped ZnO for TE waste heat recovery at high temperatures. The presence of precipitates with high number density is essential for phonon scattering, thereby reducing lattice thermal conductivity and enhancing the energy conversion efficiency. A 3 at. % super-saturated Ni-doped ZnO solid solution was prepared by sintering at 1400 °C followed by air-quenching at room temperature. Formation of nanometer to sub-micrometer size NiO-precipitates is, then, initiated by controlled nucleation and growth aging heat treatments at 750, 800, and 900 °C for different durations.

We investigate the microstructure evolution in terms of grain size, precipitate number density, average radius, and volume fraction applying electron microscopy. Thermal conductivity was determined using the laser flash analysis (LFA) technique as well as the electrical conductivity and thermopower at temperatures between 50 and 700 °C. We observed reduction of thermal conductivity at 50 °C from 18.1 W·m<sup>-1</sup>K<sup>-1</sup> in the as-quenched samples down to 17.4 and 17.6 W·m<sup>-1</sup>K<sup>-1</sup> upon aging at 750 °C for 8 and 16 h, respectively. We relate this behavior to the relatively high precipitate number density, e.g.  $1.6 \cdot 10^{20}$  m<sup>-3</sup> upon aging at 750 °C for 16 h. On the other hand, nucleation and growth of NiO-precipitates reduce electrical conductivity at 50 °C from 9.7 S·cm<sup>-1</sup> in the as-quenched specimen down to 4 and 2.2 S·cm<sup>-1</sup> upon aging at 750 °C for 8 and 24 h, respectively. The thermopower exhibits different trend, in which the as-quenched samples and those aged at 750 °C for 8 and 24 h show about the same value of 240 µV·K<sup>-1</sup> at 50 °C. In conclusion, aging heat treatments yield an overall decrease of ZT and a maximum ZT-value of 0.08 at 700 °C obtain for the as-

quenched samples. Finally, we discuss the combined effects of precipitates, impurities, and grain boundaries, on both thermal and electrical conductivities, and draw the correlation between microstructure and these transport properties in Ni-doped ZnO.

## 2. Literature review

#### 2.1 Basics of thermoelectricity

The thermoelectric (TE) effect allows direct conversion of heat to electrical energy and vice-versa. Devices that implement this effect can serve as refrigerators or power generators by waste heat recovery. <sup>1, 2</sup> Highly-efficient energy harvesting technology may lead to reduction of global fossil fuels consumption and carbon dioxide emissions. The use of TE technology offers many advantages; e.g., vibrationless cooling for opto-electronic devices and maintenance-free power generation. <sup>3</sup>

TE devices are based on the Seebeck effect, a phenomenon discovered in 1821.<sup>4</sup> The Seebeck coefficient, *S*, is defined (Eq. (1)) as the ratio of the open-circuit voltage,  $\Delta V$ , produced between two poles of a TE material when placed along a temperature difference,  $\Delta T$ .<sup>5</sup>

$$S = \frac{\Delta V}{\Delta T} \tag{1}$$

A material which exhibits a Seebeck coefficient having an absolute value at the range of 150–250  $\mu$ V/K or greater is considered to be a good candidate for TE applications. <sup>6</sup> By connecting n-type and p-type semiconducting legs to an electrical circuit a TE modules is formed. An example of a sample TE module is shown in Figure 1.<sup>7</sup>



**Figure 1.** A schematic illustration of a thermoelectric module.<sup>7</sup>

A TE device commonly comprises several TE junctions (modules), which are connected electrically in series and thermally in parallel, as shown in Figure 2.



**Figure 2.** A Schematic illustarion of a thermoelectric device, in which several TE modules are connected electrically in series and thermally in parallel. <sup>8</sup>

The three major characteristics of TE materials are the Seebeck coefficient, which should be large, the electrical conductivity,  $\sigma$ , which should be high, and the thermal conductivity,  $\kappa$ , which should be low to maintain the temperature gradient. These three requirements are embodied in the dimensionless TE *figure of merit* (ZT), where T is the absolute temperature. ZT provides a measure to evaluate TE materials performance, and is expressed in Eq. (2): <sup>5, 6, 8</sup>

$$ZT = \frac{S^2 \sigma}{\kappa} \cdot T \tag{2}$$

The product  $S^2 \sigma$  is defined as the *power factor* (PF). The dependence of the total efficiency of a TE module on material properties (ZT<sub>avg</sub>) and the temperatures difference ( $\Delta$ T) between the hot (T<sub>H</sub>) and cold (T<sub>C</sub>) sides of the module is given in Eq. (3).<sup>9</sup>

$$\eta = \frac{\Delta T}{T_H} \frac{\sqrt{1 + ZT_{avg}} - 1}{\sqrt{1 + ZT_{avg}} + \frac{T_C}{T_H}}$$
(3)

The maximum total efficiency of a module is limited by the Carnot efficiency  $\left(\frac{T_H - T_C}{T_H} \equiv \frac{\Delta T}{T_H}\right)$ . The efficiency of a Thermoelectric device as a function of  $T_H$  (heat source temperature) for various average ZT-values is shown in Figure 3. In this figure, other current heat engine devices are incorporated for comparison.<sup>3</sup>



**Figure 3.** Thermoelectric device efficiency as a function of  $T_H$  (heat source temperature) for various average ZT values.<sup>3</sup>

Nowadays the major drawback of the TE technology is insufficient energy conversion efficiency. The ZT-values of state-of-the-art commercial TE materials barely exceed 1; this limits the efficiency of TE devices to about 10-15 percent of the maximum possible Carnot efficiency. <sup>3</sup> Furthermore, the power output of the current

commercial TE devices is limited to 500 W. Achieving greater power levels up to several kW requires increasing ZT to the range of 1.5 to 3. <sup>3, 8, 10</sup>

One of the challenges in increasing the figure of merit is that improvement on one property usually causes an undesirable change in another property. For example, the thermal conductivity of materials has two components: (1) electron and hole transport component,  $\kappa_{el}$ ; and (2) lattice vibrations, i.e. phonons traveling through the lattice,  $\kappa_{ph}$ . The total thermal conductivity is then given by Eq. (4):

$$\kappa = \kappa_{el} + \kappa_{ph} \tag{4}$$

 $\kappa_{el}$  is directly related to the electrical conductivity,  $\sigma$ , according to the Wiedemann–Franz relationship. For metallic systems or degenerate semiconductors it is expressed as: <sup>11</sup>

$$\kappa_{el} = \left(\frac{\pi^2 k_B^2}{3e^2}\right) \cdot T \cdot \sigma = L_n \cdot T \cdot \sigma \quad , \tag{5}$$

where  $k_B$  is Boltzmann's constant, *e* is an electron charge, and  $L_n$  is the Lorentz number, equal to  $2.44 \cdot 10^{-8} \text{ W} \cdot \Omega \cdot \text{K}^{-2}$  for metals or heavily-doped semiconductors. <sup>5</sup> Therefore, the Wiedemann–Franz relationship introduces an inherent conflict for gaining high values of figure of merit: high electrical conductivity leads to increase of the electronic contribution to the overall thermal conductivity.

Figure 4 shows the dependence of the major TE properties on the charge carrier (holes or electrons) concentration, n. <sup>8</sup> The inverse relation between Seebeck coefficient and electrical conductivity is apparent. Compromise between S and  $\sigma$  should be made to maximize the PF. This compromise can be described in terms of effective mass of the charge carrier,  $m^*$ , and their concentration, n. According to the following expression, valid for degenerate semiconductors <sup>8</sup>

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{2/3},$$
 (6)

where *h* is Planck's constant, the Seebeck coefficient is directly proportional to the effective mass, whereas it inversely dependent on the charge carrier concentration. The electrical conductivity is expressed by:  $^{8}$ 

$$\sigma = n e \mu , \qquad (7)$$

where  $\mu$  is the charge carrier mobility. Large effective mass leads to high Seebeck coefficient. On the other hand, the effective mass is also related to the inertial effective mass, and therefore heavy charge carriers move slower due to small mobility. As a result, the electrical conductivity is reduced, according to Eq. (7). To optimize TE properties, balance between effective mass and mobility should be made. As for the charge carrier concentration, ZT is maximized typically for values ranging between  $10^{19}$  and  $10^{21}$  cm<sup>-3</sup>.<sup>8</sup>



**Figure 4.** Charge carrier concentration dependence of transport parameters required for optimum thermoelectric performance, ZT. <sup>8</sup>

Further increase of the ZT value can be obtained by lowering the lattice component of thermal conductivity. An example for optimization of ZT by controlling thermal conductivity is shown in Figure 5. At point (1) the ZT value is 0.8 and  $\kappa_{ph}$  is 0.8 Wm<sup>-1</sup>K<sup>-1</sup>. Reduction to 0.2 Wm<sup>-1</sup>K<sup>-1</sup> directly increases ZT value to point (2). Further change of the charge carrier concentrations leads to decrease in  $\kappa_{el}$ together with increase of *S*, which results in total increase of the ZT value up to point (3).



**Figure 5.** An example of ZT-optimization by controlling thermal conductivity components -  $\kappa_{ph} = \kappa_l$ .<sup>8</sup>

#### 2.2 Thermal conductivity in crystalline solids

Here we will describe the basics of thermal conductivity in crystalline solids. Then, the Callaway model will be introduced. This model is commonly applied to correlate between the materials' microstructure and their lattice thermal conductivity. This model is applied in the current study.

#### 2.2.1 Fundamentals of thermal conductivity

As mentioned above, thermal conductivity comprises of two additive terms, where the electronic one is given by Eq. (5). The lattice component,  $\kappa_{ph}$ , is given by

the following approximated expression, which is developed using the classical kinetic theory of gases: <sup>12</sup>

$$\kappa_{ph} = \frac{1}{3} \cdot C_v \cdot l \cdot v_s$$
(8)

where  $C_v$  is the constant-volume specific heat,  $v_s$  is the average sound velocity, and l is the phonon mean free path, which is defined as the average distance between two successive scattering events of a phonon traveling through the material. The efficiency of heat conduction depends on l, which is determined by the degree of phonon scattering; high scattering efficiency is manifested by short l. There are several scattering mechanisms, which are classified into either elastic/inelastic phonon-phonon interactions or phonon scattering by lattice defects, such as impurity atoms, strain fields, dislocations, stacking faults, precipitates, grain boundaries, etc. The intensity of each scattering mechanism is quantified by a characteristic relaxation time,  $\tau$ , which is the average time between two successive scattering events of the same mechanism, so that  $= \tau \cdot v_s$ . All scattering efficiencies are usually additive applying the Matthiessen rule. Herein, the equivalent inverse relaxation time,  $\tau_h$  is given by: <sup>11, 13</sup>

$$\frac{1}{\tau_t} = \sum_i \frac{1}{\tau_i},$$
(9)

At temperatures adequately lower than the Debye temperature (T<<TD),  $\kappa_{ph}$  increases as specific heat increases with temperature cube according to Debye law - T<sup>3</sup>.  $\kappa_{ph}$ reaches a peak values and then keeps decreasing at higher temperatures (T>>TD) mainly due to *Umklapp* scattering processes, which are proportional to the inverse temperature. Around the peak value,  $\kappa_{ph}$  is dominated by lattice imperfections. <sup>13</sup> A typical curve of temperature-dependent lattice thermal conductivity is demonstrated in the following figure:



**Figure 6.** The typical behavior of temperature-dependent lattice thermal conductivity.

#### 2.2.2 The Callaway model for thermal conductivity

In 1959, a phenomenological model was introduced by Joseph Callaway, aiming to describe the lattice thermal conductivity and its temperature dependence. <sup>14,</sup> <sup>15</sup> Today, this model is widely used to correlate between TE materials' microstructure and their lattice thermal conductivity. <sup>16–20</sup> The model is based on the following assumptions: <sup>14</sup>

- 1. Phonon scattering processes can be represented by frequency and temperature dependent relaxation times;
- 2. Applies for elastically-isotropic materials;
- 3. Debye-like (non-dispersive) nature of crystal vibration spectrum;
- 4. No distinction between longitudinal and transverse phonons.

For temperatures adequately higher than  $T_D$ , the following expression for lattice thermal conductivity is commonly used: <sup>14</sup>

$$\kappa_{P}\left(T\right) = \frac{k_{B}}{2\pi^{2} \nu_{s}} \left(\frac{k_{B}T}{\hbar}\right)^{3} \int_{0}^{T_{D}/T} \tau_{t}\left(x\right) \frac{x^{4} e^{x}}{\left(e^{x}-1\right)^{2}} dx$$
(10)

where  $\hbar$  is the reduced Planck constant and  $\omega$  is the phonon angular frequency. Herein, we define a dimensionless parameter:  $x \equiv \frac{\hbar \omega}{k_B T}$ .  $\tau_t$  includes contributions from different phonon scattering processes. To evaluate  $\tau_t$  in this study, the contributions of four scattering mechanisms were taken into account: (1) phononphonon inelastic interactions, which are commonly referred to as *Umklapp* (U) processes; (2) scattering by solid-solution point defects (PD); (3) scattering by precipitates (P); and (4) scattering by grain boundaries (GB).

#### 2.3 State-of-the-art TE materials and the interest in thermoelectric oxides

The most common TE materials for room-temperature up to 200 °C applications are  $Bi_2Te_3$  and  $Sb_2Te_3$  alloys. The highest ZT values for these materials are in the range of 0.8 to 1.1. For mid-temperature application (200-600 °C) materials based on group-IV-tellurides, such as PbTe, GeTe and SnTe are typically used. For both these materials groups the ZT peak value can be tuned for different temperatures by altering the charge carrier concentration. For temperatures higher than 600 °C, the most widely used TE materials are silicon-germanium compounds. Figure 7 shows the temperature-dependent ZT values for state-of-the-art commercial and recently reported n- and p-type TE materials. <sup>2</sup>

![](_page_23_Figure_3.jpeg)

**Figure 7.** The temperature-dependent ZT-values of n- and p-type compounds. The dashed lines show values for bulk state-of-the-art commercial materials, and the solid lines show recently reported values.  $^2$ 

The TE materials that are shown in Figure 7 are in commercial use and part of them exhibit ZT-values exceeding unity. However, issues such as stability at high temperature in air, volatility, toxicity, abundance, and cost are other highly-relevant factors, as well. <sup>21, 22</sup> Oxide TE materials offer several potential advantages, among them are oxidation resistance, high temperature chemical stability, low cost, and nontoxicity. The environmental friendliness and abundance of the constituent elements of oxide and non-oxide TE materials are shown Figure 8 (a) (b), respectively.

The major drawback of TE oxides is, however, their relatively low ZT-values. <sup>21, 23</sup> The development timeline of the ZT-values of TE oxides is shown in Figure 8 (c). The highest reported up-to-date ZT-value of n-type oxide are still low (0.3-0.45 at 727 °C). <sup>21–25</sup> Conversely, p-type TE oxides, such as  $Na_xCo_2O_4$  <sup>26</sup> and  $Ca_3Co_4O_9$ , <sup>27</sup> exhibit better performance with reported higher ZT-values that approach unity at 727 °C. This originates from combination of high PF and low thermal conductivities. <sup>28</sup> Improving performance of n-type TE oxide is still a challenge, and is essential for achieving efficient high temperature oxide-based TE devices.

![](_page_25_Figure_0.jpeg)

**Figure 8.** (a) Comparison between different thermoelectric materials for waste heat harvesting, in terms of the temperature range of operation, abundance, and environmental friendliness of their constituent elements. (b) The abundance of elements that are commonly present in TE materials. Elements represented by dark-colored columns exhibit abundance of <1 ppm. <sup>22</sup> (c) The development timeline of the highest ZT-values of oxide thermoelectric materials. <sup>23</sup>

#### 2.4 The interest in Zinc Oxide as a TE material

In this research we focus on TE zinc oxide (ZnO), which offers several advantages, among them are oxidation resistance, high temperature chemical stability, low cost, and non-toxicity. ZnO is intrinsically an n-type semiconducting oxide (Eg~3.3 eV at 27 °C) with a Wurtzite structure (P6<sub>3</sub>mc). <sup>29–31</sup> Synthesis of p-type ZnO is difficult, and several reasons for this are suggested. First, p-type dopants may be compensated by intrinsic deviation from stoichiometry due to lattice oxygen vacancies or Zn interstitials. Second, p-type dopants have low solubility in the ZnO crystal. Third, hydrogen atoms are present in all ZnO growth methods. These high-

mobility atoms can easily diffuse into the ZnO matrix and as "background impurities", and create negative charge compensation. <sup>31</sup> During recent years, several groups have reported on p-type conductivity of group-V (Sb, P, As) doped ZnO thin films, <sup>32</sup> and bulk materials. <sup>33</sup> Also, fabrication of nanowire p-type ZnO was demonstrated. <sup>34</sup> To the best of our knowledge, no thermoelectricity-oriented study of p-type ZnO characterization has been reported to date.

Ohtaki et al. <sup>35</sup> reported, for the first time in 1996, that polycrystalline aluminum-doped ZnO of the composition  $Zn_{0.98}Al_{0.02}O$  exhibits promising high temperature TE properties. They evaluated the thermal conductivity, electrical conductivity, and Seebeck coefficient at 1000 °C to be ca. 5.4 W·m<sup>-1</sup>K<sup>-1</sup>, 400 S·cm<sup>-1</sup>, and 180  $\mu$ V·K<sup>-1</sup>, respectively. The resulting ZT value reached about 0.3 at this temperature.

In the last few years, several studies of TE properties of transition metals-, aluminum-, and gallium-doped ZnO have been reported. <sup>21, 29, 36-41</sup> The effects of co-doping with Al and M-atoms (M= Ga, Ti, Ni, Fe, Sm, forming  $Zn_{1-x-y}Al_xM_yO$ ) were also investigated. <sup>25, 30, 42, 43</sup> Either way, improvement in electrical conductivity and Seebeck coefficient was achieved. Nevertheless, the major drawback of these n-type ZnO-based materials is their relatively high thermal conductivity values, ca. 2-10 W·m<sup>-1</sup>K<sup>-1</sup> at 700 °C. As a result, the ZT values are still low (0.3-0.45 at 727 °C) for practical applications. <sup>21, 22, 24, 25</sup>

In 2011 Jood et al. <sup>41</sup> shown that formation of a fine nanocomposite structure of Al-doped ZnO (grain size ca. 5 to 20 nm and ZnAl<sub>2</sub>O<sub>4</sub> nano-precipitates with diameters between 30 and 200 nm) leads to significant reduction of thermal conductivity down to  $\sim 2 \text{ Wm}^{-1}\text{K}^{-1}$  at 727 °C. As a result, the overall TE performance was improved. Such improvement can probably be associated to phonon scattering, as exemplified e.g. by Kim et al. <sup>16</sup> It seems that nanostructuring is a promising way for thermal conductivity reduction and enhancement of the TE properties of ZnO.

In this research we focus on the effects of precipitation on the thermal conductivity of Ni-doped ZnO. Second-phase precipitation in doped ZnO systems have already been reported, for example formation of ZnAl<sub>2</sub>O<sub>4</sub>-precipitates in an Al-doped ZnO-matrix, <sup>30</sup> and NiO-precipitates in a Ni-doped ZnO-matrix. <sup>36, 37</sup> <u>The</u>

precipitates formed in these studies were, however, generated unintentionally during the fabrication processes of the samples, and their number density, size, and volume fraction were not controlled during experimental routine. As mentioned above, a significant progress towards employment of precipitation for thermal conductivity reduction was made by Jood et al., <sup>41</sup> who investigated the two-phase microstructure evolved from a series of ZnO-based materials with different concentrations above solubility limit and its effects on TE properties.

#### 2.5 Ni-doped ZnO as a thermoelectric material

To the best of our knowledge, there are only two reports on the TE properties of Ni-doped ZnO. Colder et al. <sup>36</sup> have prepared dense ceramic specimens from Zn<sub>1</sub>. <sub>x</sub>Ni<sub>x</sub>O ( $0 \le x \le 0.06$ ) nanometric powder, that were synthesized by liquid route. Nanoparticles and highly homogeneous matrix can be achieved applying this technique. Zinc acetate dehydrate and nickel acetate tetrahydrate were dissolved and mixed in the appropriate proportion in hot ethanol. Oxalic acid was added to precipitate the Zn–Ni oxalate. The dried powder was calcinated in air at 450 °C for 2 h followed by uniaxial pressing. The compacted green bodies were sintered in air at 1400 °C for 2 h. The solubility limit of Ni in ZnO was determined to be around X=0.03 (at. fraction) by Energy Dispersive Spectroscopy (EDS) and X-ray diffraction (XRD) through lattice parameter measurements. At X=0.06, a secondary cubic structure similar to NiO was observed, Figure 9.

Park et al. <sup>37</sup> added Ni to ZnO by the dry powder (oxides) mixing method. In this report, the second cubic phase (NiO) is clearly observed for X=0.03 and higher, Figure. 10. The diffraction pattern of the NiO cubic phase along the grain boundaries is introduced by transmission electron microscopy (TEM) in Figure 11. Both papers reported that the higher the Ni content, the smaller the average grain size of the samples, possibly due to grain growth inhibition.

The secondary cubic NiO phase reported by both studies is expected to appear as an equilibrium phase, based on the ZnO - NiO phase diagram, Figure 12. 44,45

![](_page_28_Figure_0.jpeg)

**Figure 9.** Secondary electron micrographs of sintered  $Zn_{1-x}Ni_xO$  samples with X=0 (a), X=0.03 (b) and X=0.06 (c). d denotes the dense bodies' density relative to the theoretical density. The average grain size is 30.5 µm, 29 µm and 21 µm for (a), (b), and (c), respectively. <sup>36</sup>

![](_page_28_Figure_2.jpeg)

**Figure 10.** Secondary electron micrographs taken from the surface of as-sintered  $Zn_{1-x}Ni_xO$  with x=, (d) 0.03, (e) 0.04, and (f) 0.05. The white contrast marks the NiO cubic phase. <sup>37</sup>

![](_page_29_Figure_0.jpeg)

**Figure 11.** A bright field transmission electron microscopy (TEM) micrograph obtained from a  $Zn_{0.98}Ni_{0.02}O$  sample. The white arrows denote the NiO precipitates along the grain boundaries. (a) and (b) are selected area diffraction patterns taken from the  $Zn_{0.98}Ni_{0.02}O$  and NiO phases, respectively.<sup>37</sup>

![](_page_29_Figure_2.jpeg)

**Figure 12.** A phase diagram for ZnO-NiO system. <sup>44</sup> The solubility limit at 1050  $^{\circ}$ C is 0.03±0.01, adapted from A. Navrotsky and A. Muan. <sup>45</sup>

Figure 13 shows that addition of Ni, up to X=0.03, increases the electrical conductivity by more than one order of magnitude at room temperature. The charge carrier concentration determined by Hall measurements is  $1.6 \times 10^{18}$  cm<sup>-3</sup> for X=0, and 2.8  $10^{19}$  cm<sup>-3</sup> for X=0.03. Since Ni-atoms are divalent, the carrier concentration

should not change when Ni-atoms are substituting for Zn sublattice sites. The explanation that the authors provide for this finding is that Ni-substitution may slightly change the ZnO band structure and add an impurity level inside the bandgap. Decrease of electrical conductivity for Ni concentrations above X=0.03 is hardly explained in terms of microstructure changes affecting carrier mobility: "the grain size decrease involves the increase of the high resistive grain boundary surface". <sup>36</sup>

Park et al. <sup>37</sup> reported the same behavior of the electrical conductivity, i.e. maximum values at X=0.03. In this report, the decrease of conductivity above X=0.03 is attributed to increase of the amount of the NiO-phase, which has lower electrical conductivity. In both studies the absolute value of the Seebeck coefficient demonstrated the same trend as the electrical conductivity with maximum absolute value at X=0.03.

The variation of thermal conductivity with Ni concentration is shown in Figure 13. For X=0 the thermal conductivity is evaluated as 37 W·m<sup>-1</sup>K<sup>-1</sup> at room temperature. In the range of X=0.01 through X=0.03, thermal conductivity decreases down to 17 W·m<sup>-1</sup>K<sup>-1</sup>, and above X=0.03 the thermal conductivity becomes independent of the Ni concentration (~15 W·m<sup>-1</sup>K<sup>-1</sup> at room temperature for X=0.04, 0.05, 0.06), then reaches ~7 W·m<sup>-1</sup>K<sup>-1</sup> at 727 °C. As shown in the inset of Figure 13 (d), a linear relationship can be found in the thermal conductivity, when plotted on a 1/T scale, indicating that conductivity is dominated by lattice vibrations and U-processes dominate. <sup>36, 46</sup> The highest value of ZT, 0.08 at 727 °C, was obtained for Ni concentration of X=0.03 by Colder et al. <sup>36</sup> Park et al. <sup>37</sup> have not reported on thermal conductivity measurements and, therefore, did not assess ZT. We estimate a ZT-value of 0.18 at 727 °C for Park et al.'s study by combining their electrical properties with the reported thermal conductivity by Colder et al. As reviewed above, 3 at. % Ni doping level provided the optimum TE properties for the Ni<sub>1-x</sub>Zn<sub>x</sub>O system, and is chosen by us as a starting point in this study.

![](_page_31_Figure_0.jpeg)

**Figure 13.** Temperature-dependent electrical conductivity  $\sigma$  (a), Seebeck coefficient *S* (b), power factor PF (c), and thermal conductivity  $\kappa$  (d) of Ni doped ZnO and ZnO samples. <sup>36</sup>

#### 2.6 Summary

The TE effect allows direct conversion of thermal to electrical energy, and vice-versa. Highly-efficient energy harvesting by TE technology may lead to reduction of global fossil fuels consumption and carbon dioxide emissions. The three major characteristics of TE material are the Seebeck coefficient, *S*, the electrical conductivity,  $\sigma$ , and the thermal conductivity,  $\kappa$ . To obtain an efficient TE material these three characteristics should be optimized and controlled to maximize the dimensionless TE *figure of merit* (ZT).

TE oxides offer several potential advantages; among them are oxidation resistance, high temperature chemical stability, low cost, and non-toxicity. p-type TE oxide, such as  $Na_xCo_2O_4$ <sup>26</sup> and  $Ca_3Co_4O_9$ <sup>27</sup>, exhibit a reported ZT-value that approach unity at 727 °C, which is the criterion of applicability. However, the ZT-value of n-type TE oxides is still low (0.3-0.45 at 727 °C). <sup>21, 22, 24, 25</sup> Therefore, performance improvement is required.

#### 2.7 Research Objectives

The primary goal of our research is to reduce lattice thermal conductivity by the presence of precipitates with high number density values, due to phonon scattering. We hypothesize that the thermal conductivity of Ni-doped ZnO can be manipulated by altering the precipitate number density. To this end, we implement aging heat treatments that are intended to <u>control</u> the nucleation and growth of NiO-precipitates in a ZnO-matrix. This was done by aging heat treatments of super-saturated solid solution Ni-doped ZnO at 750, 800, and 900 °C for different aging times. Our secondary goal is to investigate the microstructure temporal evolution in terms of grain size, precipitate number density, average radius, and volume fraction, and to draw the correlation between microstructure and thermal conductivity for Ni-doped ZnO. Finally, we evaluate the influence of the nano/micro-structure variations upon aging heat treatments on the temperature-dependent electrical conductivity and Seebeck coefficient, striving for enhancing TE performance.

## 3. Experimental and analytical methods

#### **3.1** Sample preparation

High purity (99.99% on metals basis) ZnO powders (ABCR, Germany) with particle diameter smaller than 74  $\mu$ m (-200 Mesh – d<sub>50</sub>=1.1  $\mu$ m) was used as starting material. The ZnO powder was mixed with anhydrous ethanol to create slurry with solid load of  $\sim 25$  wt. %. Incorporation of the Ni<sup>2+</sup> was achieved by adding the required amount of nickel nitrate hexahydrate  $Ni(NO_3)_2 \cdot 6H_2O$  (Purity > 99.9% on metals basis – Spectrum, USA) salt to obtain nickel doping level of 3 at. %. Ni-free ZnO slurry was made to use as a reference material. The slurry was stirred by a Teflon magnetic stirrer in polyethylene bottle, prior to air-drying with a constant stirring rate to maintain homogeneity. The dried powder was sieved using a 150 µm (100 Mesh) sieve. The dried, granulated slurries were compacted into discs (7.2 mm dia., ~1.6 mm thick) and bars of the dimensions ca.  $2.3 \times 3.3 \times 16.5$  mm<sup>3</sup> by uniaxial pressing at ~150 MPa. The green bodies were fired at 750 °C for 1 h in air to convert the nickel-salt to NiO. Then, the samples were sintered in air at 1400 °C for 5 h to increase density and to dissolve the Ni<sup>2+</sup> in the ZnO lattice. To avoid early precipitation of the NiO-phase, we air-quenched the samples at the end of the sintering process to room temperature by pulling them immediately out of the furnace and applying forced air convection. Side-view and top-view of the quenching system can be seen in Figure 14 and Figure 15, respectively. The sintering temperature was selected to ensure complete solubility of Ni<sup>2+</sup>. <sup>36, 44, 45</sup> The quenched samples were aged in air at three different temperatures: 750, 800 and 900 °C for several durations, see Table I. Aging heat treatments were performed by placing the specimens into a pre-heated furnace followed by air-quenching. Table I provides a list of all specimens that were prepared and heat treatment details.

![](_page_34_Picture_0.jpeg)

Figure 14. A side-view of the room-temperature forced air convection quenching system.

![](_page_34_Figure_2.jpeg)

Figure 15. A top-view of the room-temperature forced air convection quenching system.

**Table I.** A summary of the specimens prepared and heat treated in the current research. As-quenched specimens are marked as '0 h'.

Composition	Aging temperature	Aging duration [h]								
	[°C]	0	2	4	5	8	16	24	33	48
ZnO		$\checkmark$								
Zn <sub>0.97</sub> Ni <sub>0.03</sub> O	900	$\checkmark$	$\checkmark$	$\checkmark$		$\checkmark$	$\checkmark$	$\checkmark$		
Zn <sub>0.97</sub> Ni <sub>0.03</sub> O	800	$\checkmark$	$\checkmark$			$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$
Zn <sub>0.97</sub> Ni <sub>0.03</sub> O	750	$\checkmark$			$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$		$\checkmark$

#### **3.2** Microstructure analysis

#### **3.2.1** X-ray diffraction (XRD)

X-ray diffraction (XRD) for phase identification was carried out using a Rigaku *SmartLab* diffractometer, applying Cu-K<sub> $\alpha$ </sub> radiation at the angular range of  $2\theta = 30-100^{\circ}$ . The data were collected with an angular resolution of 0.02 °.

#### **3.2.2** High-resolution scanning electron microscopy (HR-SEM)

Microstructure characterization of the samples was carried out using a Zeiss *Ultra Plus* high-resolution scanning electron microscope (HR-SEM) equipped with a Schottky field-emission electron gun. The images presented in this study were taken using a secondary electron detector operated at 4 keV. The chemical composition was analyzed using energy dispersive x-ray spectroscopy (EDS).

#### **3.2.3** Grain size analysis

The average grain size was estimated using the line-intercept method. <sup>47</sup> We used Stream essential OLYMPUS © software to analyse the SEM micrographs.
#### **3.2.4** Density measurements

The samples' bulk density values were calculated from measurements of the specimens' weight, *m*, using a balance with 1 mg accuracy and their volume using calipers with 0.01 mm accuracy. The density and percentage with respect to theoretical density (%TD) were calculated from Eq. (11) and Eq. (12), respectively. Here, *h* is the sample's thickness, D is sample's diameter, and  $\rho_T$  is the theoretical density of ZnO, 5.605 g·cm<sup>-3</sup>.

$$\rho = \frac{m}{h \cdot \frac{\pi D^2}{4}} \tag{11}$$

$$\% TD = \frac{\rho}{\rho_T} 100 \tag{12}$$

# 3.2.5 Precipitates number density, average radius and volume fraction evaluation.

The precipitate number density,  $N_v$ , was evaluated by counting the number of precipitates,  $n_m$ , residing on the surface of the samples having a unit area,  $A_m$ , based on SEM micrographs. Assuming that the precipitates are homogenously dispersed on the sample's surface as well as in the bulk, the average distance between precipitates, d, can be evaluated by:

$$d = \sqrt{A_m / n} \quad , \tag{13}$$

yielding a number density value of:

$$N_V = 1 / d^3 . (14)$$

The average radius of the precipitates, R, was evaluated assuming that the precipitates' cross section is circular, and calculated using the following relationship:

$$R = \sqrt{A_p / \pi} , \qquad (15)$$

where  $A_p$  is a precipitate's average surface area, which is evaluated as the surface covered by the precipitates in  $A_m$  divided by *n*. Assuming that the precipitates are spheroidal, their volume fraction is evaluated by:

$$V_f = \frac{4}{3}\pi R^3 \cdot N_V.$$
 (16)

#### **3.3** Thermoelectric characterization

Physical measurements were performed in two main categories: electrical and thermal measurements. The electrical measurements include both electrical conductivity and Seebeck coefficient (thermopower), and the thermal measurements include thermal diffusivity and heat capacity.

#### **3.3.1** Thermal conductivity measurements

The materials' thermal conductivity,  $\kappa$ , was determined by measuring their temperature-dependent thermal diffusivity,  $\alpha$ , and specific heat,  $C_P$ , as well as their density,  $\rho$ .  $\kappa$  is expressed by: <sup>5</sup>

$$\kappa(T) = \alpha(T) \cdot \rho \cdot C_p(T) . \tag{17}$$

We employ the Netzsch *Microprobe* LFA-457 laser flash analysis (LFA) system to directly measure the thermal diffusivity of disc-shaped (6 mm dia.) specimens. Technical specifications of the system are shown in Table II.

**Table II.** Technical specifications of the Netzsch *Microprobe* LFA-457 system, as are provided by the manufacturer.

Technical Specifications					
Standard Sample Holders and Possible Sample Dimension*	Ø6 mm, Ø8 mm, Ø10 mm, 0.1 mm to 6 mm sample thickness Ø12.7 mm, 0.1 mm to 6 mm sample thickness Ø25.4 mm, 0.1 mm to 6 mm sample thickness □6 mm x 6 mm, □8 mm x 8 mm, □10 mm x 10 mm, 0.1 mm to 6 mm sample thickness				
Furnaces	-125°C to 500°C (Helium atmosphere recommended) RT to 1100°C				
Laser	Nd: Glass, Energy: to 18	Nd: Glass, Energy: to 18 J, Pulse Width: 0.3 ms			
Sensors	MCT (Mercury Cadmium Telluride), LN <sub>2</sub> -cooled** InSb (Indium Antimonide), LN <sub>2</sub> -cooled**				
Thermal Diffusivity Range	0.01 mm²/s to 1000 mm²/s				
Thermal Conductivity Range	0.1 W/(m·K) to 2000 W/(m·K)				
Repeatability	Thermal Diffusivity: Specific Heat:	±2% (for standard materials) ±3% (for standard materials)			
Accuracy	Thermal Diffusivity: Specific Heat:	±3% (for most materials) ±5% (for most materials)			
Measurement atmosphere	Inert, oxidizing or vacuum (<10 <sup>-2</sup> mbar)				
Utilities	110/230 V 50/60 Hz, 16 Water 1 liter/week, LN <sub>2</sub>	110/230 V 50/60 Hz, 16 A (one 230 V line is required for the PU) Water 1 liter/week, $LN_2$ 2 liters/day			
Instrument Dimensions	Width: 570 mm, depth:	Width: 570 mm, depth: 550 mm, height: 880 mm			

The LFA method is based on a short pulse (0.5 ms) of high intensity energy that is generated by a solid-state Nd-YAG laser. The laser pulse hitting the front surface of the specimen is absorbed and propagated toward the back surface. The thermal response of the specimen is monitored by an infra-red detector. This enables us determine the temperature-dependent thermal diffusivity, assuming unidirectional heat flow, as follows: <sup>48</sup>

$$\alpha(T) = 0.1388 \frac{h^2}{t_{0.5}} , \qquad (18)$$

where  $t_{0.5}$  is the characteristic time at which the thermal signal reaches 50% of its intensity, as shown e.g. in Figure 16 (a). A schematic description of the furnace, laser source, specimen holder, and detector position is shown in Figure 16 (b).



**Figure 16.** (a) An illustration of the laser pulse, the thermal respone detected from the back-side of the specimen, and determination of  $t_{0.5}$ . (b) A schematic description of the laser flash analysis (LFA) method.

In the current experimental procedure we measure thermal conductivity in the range of 50 through 800 °C under flowing Ar atmosphere. The temperaturedependent heat capacity is simultaneously measured in the LFA by a comparative method using a pure reference  $Al_2O_3$ -sample having similar geometry.<sup>18</sup>

## **3.3.2** Determination of electrical conductivity

The Netzsch SBA-458 system enables us simultaneous measurements of both electrical conductivity and Seebeck coefficient for thin films and bulk materials having any planar geometry (ca. 10 through 25.4 mm dia.), at temperatures ranging from RT to 800 °C. Measurements are performed under flowing, high-purity (5N) Ar. As the furnace reaches a given temperature set point, a measurement of the electrical conductivity takes place using the electrical contacts. Afterwards, the two micro heaters generate a temperature difference along the sample and measurement of the Seebeck coefficient takes place. The sheet resistivity of a sample is determined using the linear four terminal arrangement method. According to Smits, <sup>49</sup> the sheet resistivity of quasi-infinite size sheets is given by:

$$\rho_r = \frac{\Delta V}{I} \frac{2\pi}{\left(\frac{1}{s_1} + \frac{1}{s_3} - \frac{1}{s_1 + s_2} - \frac{1}{s_2 + s_3}\right)},$$
(19)

where the  $s_{i}$  parameters are the spacing between the probes at the sample holder. For the present configuration, these distances are:  $s_1=s_3=1.5$  mm, and  $s_2=7.8$  mm, which leads to a simplified formula given by:

$$\rho_{r} = \frac{\Delta V}{I} \frac{2\pi}{\left(\frac{1}{s_{1}} - \frac{1}{s_{1} + s_{2}}\right)},$$
(20)

Due to the specimens' finite dimensions, scattering factors have to be considered in the calculation of the resistivity, having the form:

$$\delta_x = \Sigma A_n \cdot e^{-x/t_n}, \qquad (21)$$

where *x* stands for either the thickness, width, or length. The corrected expression for resistivity is, therefore:

$$\rho_{final} = \frac{\rho_r}{\delta_x \cdot \delta_y \cdot \delta_z}$$
(22)

The scattering factors are obtained from the theory of mirror charges in electrostatics, and usually cannot be determined analytically. Therefore, finite element analysis is

applied to determine the scattering factors for the present sample geometries, and this code is automatically applied by the SBA-458 analysis interface for a given specimen geometry. The sample thickness range for this evaluation is limited to the range of 10  $\mu$ m through 2 mm.

In the current experimental procedure we measured electrical conductivity,  $\sigma$ , for bar-shaped specimens of the dimensions of  $1.8 \times 2.5 \times 13.5 \text{ mm}^3$  in the range of 50 through 700 °C under flowing Ar atmosphere.

#### **3.3.3** Determination of the Seebeck coefficients

Measurements of the Seebeck coefficient, S, are performed using two differential thermocouples, where one of the junctions of each thermocouple is juxtaposed onto the sample, and the other junction is placed at a reference temperature TREF (both on the same TREF), as shown in Figure 17.



Figure 17. A schematic description of the SBA-458 Seebeck coefficient measurement setup.

This measurement setup allows a simple way to determine the Seebeck coefficient of a sample, since it is reduced to the configuration shown in Figure 18.



Figure 18. A typical configuration for measurement of the Seebeck coefficient.

External heaters produce a temperature difference of  $T_{1/2}$  along the sample, and the resulting voltage between these positions is probed. The Seebeck coefficient is then calculated using Eq. (23), given the Seebeck coefficient of material B (*S*<sub>B</sub>):

$$S - S_B = \lim_{\Delta T \to 0} \frac{\Delta V}{\Delta T} \quad , \tag{23}$$

where  $\Delta T \equiv T_2 - T_1$ 

In the current experimental procedure Seebeck coefficients, *S*, were measured for bar-shaped specimens of the dimensions of  $1.8 \times 2.5 \times 13.5 \text{ mm}^3$  in the range of 50 through 700 °C under flowing Ar atmosphere.

# 4. Results

In the following paragraphs the experimental results from this study are described. The first section (4.1) focuses on microstructure characterization using XRD for phase identification, HR-SEM for evaluation of grain size, precipitates number density, average radius, and volume fraction. The second and third sections (4.2 and 4.3) provide the measured thermoelectric properties including electrical conductivity, Seebeck coefficient, and thermal conductivity measurements.

### 4.1 Microstructure characterization

#### 4.1.1 X-ray diffraction (XRD) analysis

The XRD analyzes were performed first for the pure ZnO and as-quenched  $(Zn_{0.97}Ni_{0.03}O)$  to make sure that no second phase was created during the quenching process. The XRD patterns are presented in Figure 19. The diffraction pattern of the pure ZnO exhibits a Wurtzite structure of the P6<sub>3</sub>mc space group symmetry (ICDD 36-1451). The as-quenched samples show the same pattern as that observed for the pure ZnO, which means that no second phase was detected.



**Figure 19.** X-ray diffraction (XRD) patterns collected from pure ZnO (lower-marked in orange) and as-quenched  $Zn_{0.97}Ni_{0.03}O$  (higher in green).

Figure 20 (a) shows XRD patterns collected from the aged samples are shown in addition to those collected from the pure ZnO and as-quenched (AQ) samples. In contrast to the pure ZnO and as-quenched samples, the XRD patterns collected from the aged samples indicate the presence of a second phase, Figure 20 (b). This phase is attributed to a cubic NiO-base phase dissolving Zn, having the form  $Ni_xZn_yO$  (ICDD 01-71-1179). <sup>36, 37, 44</sup>



**Figure 20.** (a) X-ray diffraction (XRD) patterns collected from pure ZnO (marked in orange), as-quenched  $Zn_{0.97}Ni_{0.03}O$  (green), and the samples aged at the following conditions: 750 °C/24 h (black), 800 °C/24 h (red), and 900 °C/24 h (blue). – on logarithmic-scale (b) An inset in the 2 $\theta$ - angular range of 40 through 46 ° - on linear-scale.

#### 4.1.2 Density measurements

The density of the pure ZnO and as-quenched samples were evaluated to be  $5.19\pm0.11 \text{ g}\cdot\text{cm}^{-3}$  (92.5 %TD) and  $5.17\pm0.07 \text{ g}\cdot\text{cm}^{-3}$  (92.2 %TD), respectively. It is indicated that aging heat treatments do not affect the sample densities.

# 4.1.3 High-resolution scanning electron microscopy (HR-SEM) and energy dispersive spectroscopy (EDS) analysis

HRSEM analysis was performed for two purposes. First, as a complementary measurement to the XRD analysis, we looked for the presence of second phase precipitates which are undetectable in XRD analysis. Second, which is the main purpose, we are interested in microstructure evolution due to aging heat treatments. Precipitate number density, average radius, grain size, and volume fraction were evaluated by HRSEM micrographs and taken into account in the analysis of thermal conductivity, Chapter 5. All micrographs taken from the as-quenched and aged specimens did not undergo any surface treatment.

Micrographs of the pure ZnO and as-quenched samples are shown in Figure 21. No second phase was detected, neither at grain boundaries nor in the grain interiors.



**Figure 21** Secondary electron micrographs taken from the surface of (a) pure ZnO and (b) as-quenched  $Zn_{0.97}Ni_{0.03}O$ .

SEM micrographs taken from series of samples aged at the above three temperatures for different durations are shown in Figure 22. The white spots shown in the micrographs are identified as NiO-based precipitates. Qualitative composition analysis in precipitate-free regions was performed using EDS, indicating that Ni is dissolved in the ZnO-matrix (Figure 22e). Higher magnification SEM micrographs were taken from the aged samples, and are shown in Figure 23. Qualitative EDS composition analysis of the precipitates, shown in Figure 23 (c), confirm that the precipitates are Ni<sub>x</sub>Zn<sub>y</sub>O solid-solution.

It is noteworthy that the precipitates surface coverage fraction inside the samples (characterized by fractography - Figure 24) are dozens percent lower compared to their coverage fraction observed on the sample's free surface. This information was taken into account for evaluation of the precipitate number density.



**Figure 22.** Scanning electron microscope (SEM) micrographs (secondary electrons signal) taken from the surface of the as-processed samples aged at different conditions, as follows. (a) 750 °C/8 h, (b) 750 °C/48 h, (c) 800 °C/2 h, (d) 800 °C/24 h, (e) 900 °C/4 h, and (f) 900 °C/24 h. The white spots shown in the micrographs are identified as Ni<sub>x</sub>Zn<sub>y</sub>O precipitates. Inset in image (f) is a high-magnification image with 2  $\mu$ m scale bar. The yellow arrows designate intergranular porosity.



**Figure 23.** Scanning electron microscope (SEM) micrographs taken from the surface of the samples aged at (a) 750 °C/48 h, (b) 800 °C/24 h, and (c) 900 °C/24 h.



**Figure 24.** A scanning electron microscope (SEM) micrograph taken from the surface of an intra-granular fracture of the sample aged at 800 °C for 24 h. The yellow arrows designate precipitate-covered regions on the fracture surface.

# 4.1.4 Grain size ,precipitates number density, average radius, and volume fraction evaluation

The precipitate number density, average radius, volume fraction, and average grain size that were evaluated for the aged samples are shown in Figure 25. After 2 h aging heat treatment at 900 °C, a precipitate number density value of  $1.8 \cdot 10^{17}$  m<sup>-3</sup> and average radius of ~85 nm were observed. A longer aging heat treatment for 4 h maintained the average radius, while the number density increased by more than an order of magnitude, reaching at a maximum value of  $7.5 \cdot 10^{18}$  m<sup>-3</sup> for the samples aged at 900 °C. Further aging increased the precipitate volume fraction mainly due to precipitate growth; the average radius reached up to ~110 nm after 24 h.

Reducing the aging heat treatment temperature to 800 °C led to a rise of the number density value by about an order of magnitude after 2 h aging. Additionally, the precipitate number density increased steadily with aging time, and reached values as great as  $1.4-2.1\cdot10^{18}$  m<sup>-3</sup>. The average radius obtained after 2 h aging decreased down to ~ 40 nm, which is about 50 % lower than those observed for the samples aged at 900 °C.

After aging at 750 °C for 5 h, further decrease of the precipitates' average radius down to ~ 30 nm was observed. 8 h aging at this temperature yielded a number density value as great as  $3.1 \cdot 10^{19}$  m<sup>-3</sup>, which is the largest value compared to those observed at the same aging time for the other temperatures. A maximum number density of  $1.6 \cdot 10^{20}$  m<sup>-3</sup> was observed after 48 h at 750 °C. Figure 25 (d) indicates that aging heat treatments do not affect significantly the average grain size.



**Figure 25.** Temperature and time dependence of (a) precipitate number density,  $N_{\nu}$ . (b) precipitate volume fraction, V<sub>f</sub>, (c) precipitate average radius, R, and (d) average grain size, L, shown for pure ZnO (marked in orange circles), as-quenched (green circles), and the samples aged at 750 °C (black squares), 800 °C (red circles), and 900 °C (blue triangles).

#### 4.2 Thermal conductivity measurements

The thermal conductivities of pure ZnO, as-quenched, and the aged samples were calculated based on Eq. (17). The temperature dependent thermal diffusivities were measured directly by LFA in the range of 50 through 700 °C under flowing Ar atmosphere. The samples' density was evaluated at room temperature from their dimensions and weight, and are considered to be constant. The temperature dependent heat capacity is measured in a comparative method using a pure  $Al_2O_3$  reference sample having similar geometry. The heat capacity values for some

representative samples are shown in Figure 26. We interpolate a representative average  $C_p(T)$ -function for all the samples, Figure 27, to apply it for the temperature-dependence thermal conductivity calculations.



**Figure 26.** Temperature-dependent heat capacity values measured for several samples: pure ZnO (marked in orange dimonds), as-quenched (red circles), and the aged samples at (a) 900 °C and (b) 750 °C.



**Figure 27.** An interpolated function for temperature-dependent heat capacity, representative for all specimens.

The thermal conductivity of the pure ZnO, the as-quenched, and the aged samples as a function of the temperature is presented in Figure 28. At 50 °C, all of the Ni-alloyed materials, namely, the as-quenched and aged samples, exhibit a significant reduction of thermal conductivity, by ca. 50 %, with respect to the pure ZnO material. For example, the thermal conductivity featured by the as-quenched sample is 18.1 W·m<sup>-1</sup>K<sup>-1</sup>, compared to that of the pure ZnO, that is, 40.7 W·m<sup>-1</sup>K<sup>-1</sup>.

Since the lattice component of thermal conductivity,  $\kappa_p$ , is highly affected by lattice imperfections, such as atom impurities and micro/nano-structure variations, <sup>13</sup> we expect to observe differences between the thermal conductivities of the samples aged at different conditions. This is bacause aging initiates nucleation of Ni-rich precipitates concurrently with reducing the level of Ni-supersaturation in the ZnOmatrix. We, therefore, plot all thermal conductivity values at 50 °C to emphasize the differences between the as-quenched and the aged states, Figure 28 (d) through (f). A general trend of increase of thermal conductivity with aging time is observed for both temperatures of 900 and 800 °C, with minimum values for the as-quenched materials, Figure 28 (d) and (e). Interestingly, the samples aged at 750 °C exhibit a different trend: the thermal conductivity values decrease up to 8 h aging, then increased for longer aging times, Figure 28 (f). It should be noted that this different trend can also be seen in the measured thermal diffusivity of these samples, as presented in Figure 29. We elucidate these different trends in terms of interplay between the effects of super-saturated ZnO matrix and precipitation of the NiO-phase, to be discussed further below.



**Figure 28.** Temperature-dependent thermal conductivity measured for pure ZnO (orange dimonds), as-quenched (red circles), and the aged samples at (a) 900  $^{\circ}$ C (b) 800  $^{\circ}$ C, and (c) 750  $^{\circ}$ C. Thermal conductivity at 50  $^{\circ}$ C of as-quenched (red bars) and

the samples aged at (d) 900 °C, (e) 800 °C, and (f) 750 °C (blue bars). The error bars are evaluated based on the thermal diffusivity measurement's accuracy,  $\pm 3\%$ .



**Figure 29.** Temperature-dependent thermal diffusivity measured at 50 °C of asquenched (red bar) and the samples aged at 750 °C (blue bars). The error bars are evaluated based on the thermal diffusivity measurement's accuracy,  $\pm 3\%$ .

### 4.3 Electrical measurements

#### 4.3.1 Electrical conductivity measurements

The temperature dependence of electrical conductivity for the pure ZnO, asquenched, and series of samples aged at 750 °C are shown in Figure 30. All samples exhibit a semiconducting behavior for the entire temperature range, as expected, indicated by the trend of increasing conductivity with temperature. <sup>50</sup> The asquenched samples show the highest electrical conductivity values, e.g. 17.9 S·cm<sup>-1</sup> at 700 °C, whereas the pure ZnO samples possess the lowest values throughout the entire temperate range. It is also shown in Figure 30 that the longer the aging time is, the lower is its electrical conductivity. We associate this behavior to variations in the ZnO-matrix composition with aging time, to be discussed further below.



**Figure 30.** Temperature-dependent electrical conductivity measured for pure ZnO (orange dimonds), as-quenched (red circles), and series of samples aged at 750 °C.

### 4.3.2 Seebeck coefficient measurements

The Seebeck coefficient was measured at the range of 50 through 700 °C under flowing Ar atmosphere. The temperature dependent Seebeck coefficient results are presented in Figure 31. It can be seen that all samples exhibit negative S-values, implying on their n-type nature. The pure ZnO samples show the highest absolute Seebeck coefficient values, e.g. 517  $\mu$ V·K<sup>-1</sup> at 700 °C, whereas the as-quenched samples possess the lowest absolute values throughout the entire temperate range. In addition, it can be seen in Figure 31 that the longer the aging time is, the higher is the absolute Seebeck coefficient value. We associate this trend to the temporal evolution of the ZnO-Matrix composition with aging time, to be discussed further below.



**Figure 31.** Temperature-dependent Seebeck coefficiant measured for pure ZnO (orange dimonds), as-quenched (red circles), and series of samples aged at 750 °C

# 5. Discussion

### 5.1 Analysis of the microstructure evolution

Microstructure evolution of aged super-saturated solid solution can usually be described by three stages. <sup>51, 52</sup> The first one is precipitate nucleation at a constant rate. At this stage the rate of nucleation mainly depends on two parameters: the energy barrier for nucleation and the rate of mass transport. The second stage includes precipitate growth, and strongly depends on mass transport rate and the solubility in the matrix. Here, an individual precipitate's radius depends on aging time (t) as:  $t^{1/2}$ . The third stage is coarsening, which is driven by differences in the chemical potential of the solute atoms at the vicinity of matrix/precipitate interfaces due to their different curvature. This leads to increase of precipitates shrink and, eventually, disappear. At the coarsening stage the precipitate radius grows and depends on aging time as:  $t^{1/3}$ . Usually, these three stages overlap, with some exceptions. <sup>51, 53</sup>

We analyze the microstructure evolution observed in this study in view of the above mechanisms. The precipitate number density values shown in Figure 25 (a) indicate the following general trends. First, the maximum number density values increase with decreasing temperatures. This is associated to the energy barrier for nucleation, which is inversely-proportional to the degree of supercooling squared. <sup>52</sup> This trend is accompanied by increase of the average precipitate radius with temperature due to increasing diffusion rate; both trends are clearly indicated in Figure 32.



**Figure 32.** The temperature dependent average precipitate number density,  $\langle N_{\nu} \rangle$  (red bars), and average precipitate average radius,  $\langle R \rangle$  (blue bars).

Second, the times at which precipitate number density attains its maximum value, which indicate the onset of coarsening regime, become longer for lower aging temperatures. This is associated to diffusion rate of the Ni solute atoms in the ZnOmatrix, which strongly depends on temperature. <sup>52, 54</sup> Consequently, the onset of coarsening can be easily distinguished for the samples aged at 900 °C, i.e. between 4 and 8 h, whereas the samples aged at 750 and 800 °C, apparently, have not reached the coarsening regime yet. Quantitatively, Figure 25 (a) indicates that the number density of the samples aged at 900 °C reaches a maximum value of  $7.5 \cdot 10^{18}$  m<sup>-3</sup> after 4 h aging, and then decreases moderately with time. Conversely, the samples aged at 800 and 750 °C exhibit a nearly monotonous rise of number density, which corresponds with their precipitate volume fraction values that do not reach saturation, Figure 25 (c). It is also indicated in Figure 25 (a) that the maximum number density values observed for the samples aged at 800 and 750 °C are  $2.1 \cdot 10^{19}$  m<sup>-3</sup> (after 24 h) and  $1.6 \cdot 10^{20}$  m<sup>-3</sup> (after 48 h), respectively. The latter is essentially the greatest number density values achieved in this study. For comparison, purpose we evaluate the maximum precipitate number density obtained by other reported studies of ZnObased systems. Values of  $\sim 8 \cdot 10^{18}$  m<sup>-3</sup> and  $\sim 4 \cdot 10^{18}$  m<sup>-3</sup> for ZnAl<sub>2</sub>O<sub>4</sub>-precipitates in an

Al-doped ZnO-matrix are evaluated by us based on the micrographs reported by Jood et al. <sup>41</sup> and Yamaguchi et al., <sup>30</sup> respectively. Additionally, a number density of  $\sim 3 \cdot 10^{18}$  m<sup>-3</sup> for NiO-precipitates in a Ni-doped ZnO-matrix is estimated based on Park et al. <sup>37</sup> We highlight that the maximum number density value reported by us is considerably high compared to the aforementioned studies, since we utilized controlled aging conditions aimed at achieving enhanced N<sub>v</sub>-values.

It should be noted that evaluation of the precipitate volume fraction in this study is based on a spheroidal precipitate approximation; however, Figure 23 indicates that this assumption is a rough approximation only. This, in addition to the fact that volume fraction is calculated based on two measured values, each one having its own evaluation error, probably leads to poor accuracy in determination of the precipitate volume fraction, with a relative average error of 63 %, compared to the other magnitudes that appear in Figure 25. Conversely, the error in determination of the precipitate number density is based on counting statistics.

The maximum precipitate volume fractions that were evaluated for the aged samples at 750, 800 and, 900 °C are ca. 0.039, 0.014, and 0.028, respectively. For the sake of comparison, we evaluated the maximum NiO volume fraction at 750 and 800 °C based on the phase diagram (Figure 12) that was reported by Roy et al. <sup>44</sup> and obtained values of ca. 0.025 and 0.02, respectively. We note that the above-estimated volume fractions are expected to decrease with temperature. This is, however, true for fully-equilibrated systems, whereas the aged alloys reported in this study are in different off-equilibrium states.

## 5.2 Thermal and electrical conductivity analyses

The temperature-dependent thermal conductivity results shown in Figure 28 indicate that Ni<sup>2+</sup> dissolution in the ZnO matrix reduces thermal conductivity by ca. 50% at 50 °C with respect to pure ZnO. Colder et al. reported a similar behavior. <sup>36</sup> The thermal conductivity of pure ZnO at 50 °C as measured by us is 40.7 W·m<sup>-1</sup>K<sup>-1</sup>, in close correspondence with other reported values e.g. by Cheng et al. <sup>55</sup> (~37.5 W·m<sup>-1</sup>K<sup>-1</sup>), Tsubota et al. <sup>56</sup> (~47.0 W·m<sup>-1</sup>K<sup>-1</sup>), and Colder et al. <sup>36</sup> (~37.0 W·m<sup>-1</sup>K<sup>-1</sup>). The minimum thermal conductivity value measured in this study was obtained for

the samples aged at 750 °C for 8 h, that is, 8.0  $W \cdot m^{-1}K^{-1}$  at 700 °C. This value is slightly larger than 7  $W \cdot m^{-1}K^{-1}$  as reported by Colder et al. for the same composition (Zn<sub>0.97</sub>Ni<sub>0.03</sub>O), which was prepared by different methods. <sup>36</sup>

The samples aged for 8 and 16 h at 750 °C yielded the lowest thermal conductivity values compared to the other samples investigated. These minimum values correspond with the greatest precipitate number density values, observed for the same temperature and aging times, as shown in Figure 25 (a). To figure out whether these low thermal conductivities can be associated to phonon scattering by precipitates of high number density, we should first validate that thermal conductivity is dominated by phonons (lattice component) rather than charge carriers (electronic component). To this end, we apply the Wiedemann-Franz relationship, stating that the electronic component of thermal conductivity is proportional to the electrical conductivity at a constant temperature as shown in Eq. (5).

The calculated lattice and electronic components of thermal conductivity for the pure ZnO, as-quenched, and series of samples aged at 750 °C are plotted as a function of temperature, Figure 33, which indicates three main meaningful features. First, the electronic components of thermal conductivity are lower by 3-6 orders of magnitude than the lattice component, depending on aging time. This remarkable difference justifies drawing the correlation between thermal conductivity and microstructure in terms of phonon scattering, to be followed in Section 5.3. Second, the as-quenched (Ni-alloyed) samples show the highest  $\kappa_e$ -values, whereas the pure ZnO samples possess the lowest values throughout the entire temperature range. Also, the longer the aging time is, the lower is its  $\kappa_e$ -value. Such trend is also shown for electrical conductivity, Figure 30. These trends can be elucidated in view of the concentration of Ni-atoms that are dissolved in the ZnO-matrix. Since Ni-dopants act as electron donors, effectively, <sup>36</sup> their absence yields the lowest electrical conductivity and ke-values. This occurs in the pure ZnO samples. Conversely, the Nidoped as-quenched materials contain the highest concentration of Ni in the supersaturated ZnO matrix, i.e. above solubility limit. For this reason, this material exhibits the highest electrical conductivity and  $\kappa_e$ -values. For the thermally aged specimens, formation of NiO-precipitates reduces the Ni-concentration in the ZnO-

matrix, until it reaches its equilibrium concentration for long aging times. This explains why electrical conductivity and  $\kappa_{e}$ -values decrease with aging time. Third, it is shown that the  $\kappa_{p}$ -values decrease with increasing temperature, whereas the  $\kappa_{e}$ -values exhibit the opposite trend. Similarly, electrical conductivity increases with temperature, as shown in Figure 30. Whereas the decrease of  $\kappa_{p}$ -values with temperature can be associated to phonon-phonon Umklapp scattering (to be discussed in Section 5.3), <sup>57</sup> the increase of  $\kappa_{e}$ -values with temperature can be associated to high Ni-doping level, which yields a metal-like behavior. <sup>50</sup>



**Figure 33.** The calculated temperature-dependent lattice and electronic components of thermal conductivity,  $\kappa_p$  and  $\kappa_e$ , respectively, for pure ZnO (orange diamonds), asquenched (AQ, red circles), and series of samples aged at 750 °C for different durations. These values are calculated applying the Wiedemann-Franz relationship for the electrical conductivity results in Figure 30.

Finally, the temperature-dependent electrical conductivity of the pure ZnO, asquenched, and series of samples aged at 750 °C shown in Figure 30 indicate that the greatest value is 17.9 S·cm<sup>-1</sup> at 700 °C, and is attained for the as-quenched sample. This value is lower compared to other reported results, e.g. by Park et al., <sup>37</sup> (~65 S·cm<sup>-1</sup>) and Colder et al., <sup>36</sup> (~30 S·cm<sup>-1</sup>). We associate this difference to the relatively low density measured for the specimens in this study, as low as  $4.88\pm0.12$  g·cm<sup>-3</sup> (87.1 % TD). For comparison, Colder et al. <sup>36</sup> reported on 94.3 % TD.

## 5.3 Effects of microstructure evolution on thermal conductivity

We study the effects of microstructure, particularly NiO-precipitates, on the lattice thermal conductivity in the framework of the Callaway model, <sup>14, 15</sup> which is a common method to describe the effects of defects on a material's lattice thermal conductivity. <sup>16–20</sup> Our main purpose in applying the Callaway model is to distinguish between the effects of each scattering mechanism on the thermal conductivity. In particular, its dependence on NiO-precipitates' number density and the concentration of Ni<sup>2+</sup> dissolved in the ZnO-matrix, as well as to comprehend the interplay between these effects.

We calculated the temperature-dependent thermal conductivity of ZnO in either its pure state or including the aforementioned lattice defects applying Eq. (10). For each aging temperature and time, the microstructural features shown in Figure 25, namely precipitate number density, average radius, volume fraction, and average grain size, are employed to calculate the inverse relaxation time for the relevant scattering mechanisms. The inverse relaxation time for U-processes,  $\tau_U^{-1}$ , is expressed by <sup>58</sup>

$$\tau_U^{-1} \approx \frac{\hbar \gamma^2}{\bar{M} v_s^2 T_D} \omega^2 T e^{\left(-\frac{T_D}{3T}\right)},$$
(24)

where  $\gamma$  is the Grüneisen parameter that reflects the degree of lattice anharmonicity <sup>59</sup>, and  $\overline{M}$  is the average atomic mass of the compound. For the solid-solution PD mechanism two aspects should be concerned regarding the impurity atoms, namely the average PD/matrix mass and radius difference. The inverse relaxation time,  $\tau_{PD}^{-1}$ , is expressed by: <sup>60–62</sup>

$$\tau_{PD}^{-1} \approx \frac{\delta^3}{4\pi v_s^3} \omega^4 \Gamma, \qquad (25)$$

where  $\delta$  is the atomic volume of the impurity atom and  $\Gamma$  is the disorder parameter, which depends on mass difference and strain field exerted by the impurity atoms, as follows, <sup>62</sup>  $\Gamma = \Gamma_M + \Gamma_S$ . The mass difference is expressed by:

$$\Gamma_{M} = \frac{\sum_{i=1}^{n} c_{i} \left(\frac{\overline{M}_{i}}{\overline{M}}\right)^{2} f_{i}^{1} f_{i}^{2} \left(\frac{M_{i}^{1} - M_{i}^{2}}{\overline{M}_{i}}\right)^{2}}{\left(\sum_{i=1}^{n} c_{i}\right)},$$
(26)

where  $c_i$  is the relative degeneracies (Here  $c_1=c_2=1$ ), and  $\overline{M}$  is the average atomic mass of the compound. In the case of two different atoms at the i-th sublattice we employ:  $M_i^1$  and  $M_i^2$  for the atomic masses and  $f_i^1$  and  $f_i^2$  for the fractional concentrations. Herein, we used the following relations:  $f_i^1 + f_i^2 = 1$  and  $\overline{M}_i \equiv$  $M_i^1 f_i^1 + M_i^2 f_i^2$ . Also, the fractional concentration of the Ni atoms at the Zn-sublattice was evaluated based on the NiO-precipitate volume fraction estimated for the aged samples. The strain field factor due to the differences of impurity/matrix atomic radius is expressed by

$$\Gamma_{S} = \frac{\sum_{i=1}^{n} c_{i} \left(\frac{\overline{M}_{i}}{\overline{M}}\right)^{2} f_{i}^{1} f_{i}^{2} \varepsilon_{i} \left(\frac{r_{i}^{1} - r_{i}^{2}}{\overline{r_{i}}}\right)^{2}}{\left(\sum_{i=1}^{n} c_{i}\right)},$$
(27)

where  $r_i^1$  and  $r_i^2$  are the impurity/matrix atomic radii and  $\bar{r}_i \equiv r_i^1 f_i^1 + r_i^2 f_i^2$ .  $\varepsilon_i$  is a phenomenological adjustable parameter that typically ranges between 10 and 100<sup>60–63</sup>. Herein, we utilized a value of:  $\varepsilon_i$ =95. This value is chosen based on the measured reduction, ca. 50%, of thermal conductivity at 50 °C for the as-quenched samples

with respect to the pure ZnO material. We assume that the PD mechanism dominates for such case, since the temperature is relatively low to enable U-processes. Moreover, the effects of precipitates (if exist) and grain boundaries are identical for both material states.

To account for phonon-precipitates (P) interaction, the inverse relaxation time,  $\tau_p^{-1}$ , is expressed by: <sup>16, 61, 64, 65</sup>

$$\tau_{P}^{-1} \approx v_{s} \left(\sigma_{R}^{-1} + \sigma_{G}^{-1}\right)^{-1} N_{V},$$
(28)

where the terms  $\sigma_R$  and  $\sigma_G$  signify the effective scattering cross-sections due to the Rayleigh and near-geometrical mechanisms, respectively. These terms are expressed as:

$$\sigma_{R} = \pi R^{2} \frac{4}{9} \left( \frac{\Delta D_{m}}{D_{m}} \right)^{2} \left( \frac{\omega R}{v_{s}} \right)^{4},$$
(29)

and:

$$\sigma_G = 2\pi R^2 ; \qquad (30)$$

where  $D_m$  is the matrix density and  $\Delta D_m$  is the density difference between the precipitates (here: 6.67 g·cm<sup>-3</sup>) and matrix (5.17 g·cm<sup>-3</sup>), and *R* and  $N_v$  are the precipitates average radius and number density, respectively. For GB scattering, the inverse relaxation time,  $\tau_{GB}^{-1}$ , is approximated by: <sup>66</sup>

$$\tau_{GB}^{-1} \approx \frac{V_s}{L} \tag{31}$$

where L is an average grain size. Finally, the equivalent inverse phonon relaxation time,  $\tau_t^{-1}$ , is expressed by the Matthiessen rule <sup>11</sup>:

$$\tau_t^{-1} = \tau_{PD}^{-1} + \tau_U^{-1} + \tau_{GB}^{-1} + \tau_P^{-1}$$
(32)

we employed the following additional parameters: the Debye temperature of the ZnO-matrix,  $T_D=416$  K, <sup>67</sup> its Grüneisen parameter  $\gamma =1.7$ , <sup>68</sup> and  $v_s=3154.4$  m·s<sup>-1</sup>. <sup>69</sup> Then, the simulated thermal conductivity is calculated by combining these four scattering mechanisms into an equivalent inverse phonon relaxation time for a specific aging temperature and time. Finally, all calculated results are normalized by the thermal conductivity calculated for pure ZnO at 50 °C, and the resulting values are defined as *relative thermal conductivity*,  $\kappa_{rel}$ . The calculated relative thermal conductivity results are shown in Figure 34.



**Figure 34.** The relative temperature-dependent thermal conductivity calculated for pure ZnO (orange diamonds), as-quenched (red circles), and the samples aged at (a) 900 °C, (b) 800 °C, and (c) 750 °C for different times. The relative thermal conductivity,  $\kappa_{rel}$ , values calculated at 50 °C for the as-quenched (AQ, red bars) and the samples aged at (d) 900 °C, (e) 800 °C, and (f) 750 °C (blue bars).

In the experimental results a general trend of increasing thermal conductivity with aging time is shown for the samples aged at 900 and 800 °C, Figure 28 (d) and (e). Comparison between the calculated, Figure 34 (d and e), and experimental results, Figure 28 (d and e), for the samples aged at 900 and 800 °C, reveals a similar general trend of increasing thermal conductivity with aging time. We associate this trend to the Ni<sup>2+</sup> depletion in the ZnO-matrix, which occurs simultaneously with the formation of the NiO-precipitates during the aging heat treatment. The measured thermal conductivity for the samples aged at 750 °C exhibits a slight decrease of thermal conductivity up to 8 h aging, followed by an increase for longer aging times, Figure 28 (f). The slight decrease of the thermal conductivity for the samples aged for 5 and 8 h at 750 °C can be associated to their relatively high precipitate number density, that is,  $3.1 \cdot 10^{19}$  m<sup>-3</sup> and  $1.6 \cdot 10^{20}$  m<sup>-3</sup>, respectively. Furthermore, the calculated results for these samples, Figure 34 (f), shows that the relative thermal conductivity does not decrease; alternatively, the increasing trend that is observed for the other two temperatures is being hindered. Based on the experimental and calculated results, it turns out that the solid-solution scattering mechanism is balanced by the precipitate scattering mechanism.

Another feature arising from comparison between the calculated and experimental results at 50 °C as displayed in Figure 34 (d, e, and f) and Figure 28 (d, e, and f) is that all samples aged at 800 °C apparently obey the same trend. Particularly, thermal conductivity increases moderately with the aging time. Another similarity between experiment and calculated results for this aging temperature is the extent of thermal conductivity reduction with temperature. Both experimental and computational results exhibit reduction of ca. 50% from 50 to 700 °C.

Interestingly, the calculated results for the samples aged at 750 and 900 °C exhibit a "leap" in the relative thermal conductivity for those aged for 16 and 4 h, respectively, and for longer aging times. The origin of these calculated results lays in the inverse relaxation time for the solid-solution scattering mechanism,  $\tau_{PD}^{-1}$ . This expression is strongly dependent on the Ni<sup>2+</sup> concentration in the ZnO-matrix, and the latter is evaluated based on experimental results for NiO-precipitate volume

fractions that are relatively high for the samples aged at 750 and 900 °C for 16 and 4 h, respectively, as well as for longer aging times.

The two other phonon scattering sources considered in this system are grain boundaries and U-processes. The average grain size is shown in Figure 25 (d), indicating values between 16 and 20 µm for all samples. These values yield an estimated characteristic relaxation time of  $\tau_{GB} \approx 6$  ns. Similarly, the characteristic relaxation times for U-processes at a  $Zn_{0.97}Ni_{0.03}O$ -matrix that are estimated for 0.2  $\omega_D$  are:  $\tau_U \approx 0.59$ , 0.28, and 0.18 ns for 50, 400, and 700 °C, respectively; where  $\omega_D$ is the Debye frequency. As temperature increases, relaxation time decreases; hence, U-processes become dominant at high temperatures. 58 Both calculated and experimental results show that U-processes affect all samples to the same extent; furthermore, the relaxation time due to GB scattering is equal for all samples. We, therefore, disregard both these scattering mechanisms in our analysis of the thermal conductivity dependence on microstructure evolution. Inversely, thermal conductivity is governed by the interplay between the two other mechanisms, namely precipitate and point defect scattering, and is directly dictated by microstructure evolution. To help us differentiate between the roles of the above scattering mechanisms, we calculated the relaxation times at 50 °C as a function of the normalized phonon frequency  $(\omega / \omega_p)$ , Figure 35. To represent the experimental conditions prevailing in the current study reliably, we substitute typical values of solute concentration, precipitate number density, etc. as measured in this study in Eq. (24), (25), (28), and (31).



**Figure 35.** The relaxation times at 50 °C calculated for U-processes (black squares), point defects for as-quenched samples (red circles), precipitates for  $N_v = 1.6 \cdot 10^{20} \text{ m}^{-3}$  (blue triangles), and the total relaxation time (dashed green line), plotted against the normalized phonon frequency.

It is indicated that precipitates provide the most significant contribution for phonon scattering at low frequencies, while U-processes predominate at the mid- to high- frequency regime. Considering the P- and PD-mechanisms, which are valid for lattice imperfections, and disregarding U-processes, which apply for the perfect crystal, we can infer from Figure 35 that the P- and PD-mechanisms compete with each other, whereas the P-mechanism predominates for low phonon frequencies and the PD-mechanism predominates for high frequencies. Quantitatively,  $\tau_p$  is larger by a factor of five compared to  $\tau_{PD}$  for high frequencies. To enhance the effects of the precipitate scattering mechanism, their number density values should be increased by at least two orders of magnitudes, up to  $10^{22}$ - $10^{23}$  m<sup>-3</sup>, as predicted by Amouyal for a different system.<sup>18</sup>

Finally, we highlight that the basic hypothesis made in this study, stating that the thermal conductivity of Ni-doped ZnO can be tuned by formation of NiO-precipitates, should be treated with care. Relying on comparison between

experimental observations and computational results, it was found that solute atoms in the matrix play a significant role in phonon scattering, as well. Besides temporal evolution of the microstructure itself, one should keep in mind that the matrix concentration also varies with aging time and affects both vibrational and electronic properties.

#### 5.4 Effects of heat treatments on Seebeck coefficients

The temperature-dependent Seebeck coefficients of the pure ZnO, as-quenched, and series of samples aged at 750 °C are shown in Figure 31. The pure ZnO samples show the highest Seebeck coefficient absolute values, while the as-quenched samples show the lowest absolute values throughout the entire measured temperature range. Furthermore, the longer the aging time is, the higher is its absolute values. We associate these trends to the concentration of Ni-atoms that are dissolved in the ZnOmatrix. Since Ni-dopants act as electron donors, effectively, <sup>36</sup> their absence yields the lowest charge carrier concentration in our system. According to Eq. (6) the Seebeck coefficient is inversely dependent on the charge carrier concentration; therefore, the pure ZnO samples exhibit the highest values. In contrast, the asquenched samples exhibit the highest concentration of Ni-atoms dissolved in the ZnO-matrix, thus the highest electron concentration, Eq. (7). Consequently, these samples show the lowest Seebeck coefficient absolute values. As for the aged samples, the formation of NiO-precipitates depletes the Ni<sup>2+</sup> from the ZnO-based matrix. As a result, the electron concentration decreases. This leads to increase of the Seebeck coefficient absolute values with aging time.

The greatest absolute value of 517  $\mu$ V·K<sup>-1</sup> is achieved for the pure ZnO samples at 700 °C, which corresponds with those of intrinsic semiconductors. The value is higher compared to other reported results. e.g. by Park et al. <sup>37</sup> (~200  $\mu$ V·K<sup>-1</sup>), Colder et al. <sup>36</sup> (~310  $\mu$ V·K<sup>-1</sup>), and Ohtaki et al. <sup>46</sup> (~330  $\mu$ V·K<sup>-1</sup>). Conversely, comparison between the as-quenched samples to other reported results with the same composition, which were prepared by different methods, shows the opposite trend. The value of the as-quenched samples (308  $\mu$ V·K<sup>-1</sup>) is lower compared to the others. E.g. by Park et al. <sup>37</sup> (~450  $\mu$ V·K<sup>-1</sup>) and Colder et al. <sup>36</sup> (~410  $\mu$ V·K<sup>-1</sup>).

#### 5.5 The TE dimensionless figure of merit, ZT

The calculated temperature-dependent ZT of the pure ZnO, as-quenched, and series of samples aged at 750 °C are presented in Figure 36. It can be seen that the asquenched samples exhibit the highest ZT values throughout the entire temperature range. It starts with a value of 0.001 at 50 °C and rises till 0.02 at 700 °C, its greatest value. In contrast to this, the pure ZnO samples exhibit the lowest values from 50 to 700 °C. As for thermally aged samples, the longer the aging time is, the lower the ZT-values are. For instance, the reduction in ZT-values at 50 °C from the asquenched to the aged samples varies from tens percent for the 8 h aged samples up to 2-3 orders of magnitude for the 48 h aged samples.



**Figure 36.** Temperature-dependent TE figure of merit, ZT, evaluated for pure ZnO (orange dimonds), as-quenched (red circles), and series of samples aged at 750 °C.

It should be pointed out that the samples' ZT-values show the same general trends as the electrical conductivity results do. We associate this behavior to the significant decrease of electrical conductivity for the aged samples, as shown in Figure 30. This is because the reduction of electrical conductivity, as a result of aging heat treatment, is in order of tens percent to a few orders of magnitude. Changes in Seebeck coefficient (Figure 31) and thermal conductivity (Figure 28)

values due to aging heat treatments are, however, only as small as a few to tens percent.

Comparison between the best achieved TE properties in this study to other reported results, which were prepared by different methods, is presented in Table III. The ZT-value of 0.02 at 700 °C is lower by 75 % compared to the reported value by Colder et al. <sup>36</sup> This difference is related to the lower values that are obtained for the Seebeck coefficient and electrical conductivity mainly. We estimate a ZT-value of 0.18 at 727 °C for Park et al. <sup>37</sup> based on their electrical properties with the reported thermal conductivity by Colder et al. <sup>36</sup> The estimated ZT-value is higher by more than two times than the value obtained by Colder et al. <sup>37</sup>

In conclusion, formation of NiO-precipitates as found in this study does not contribute to achieve better TE conversion efficiency as far as we witness in our SEM analysis. The slight reduction in thermal conductivity that is obtained for the samples aged for 8 and 16 h at 750 °C is not as significant as the reduction of electrical conductivity due to NiO-precipitation. Finally, the overall ZT-value decreases with aging time. It turns out that the Ni-atoms dissolved in the ZnO-matrix significantly affect the electronic properties of this system and should be carefully taken into account, while better TE conversion efficiency is the ultimate goal.

**Table III.** A summary of the main TE properties at 700 °C in this study in comparison to other reported results, which were prepared by different methods. \* ZT is estimated using Colder et al.'s <sup>36</sup> reported thermal conductivity.

Ni 3% at. @ 700 °C	Міп. <i>к</i> [W·m <sup>-1</sup> К <sup>-1</sup> ]	Max.  S  [μV·K <sup>-1</sup> ]	Max. σ [S·cm <sup>-1</sup> ]	Max. ZT
This study	8	308	17.9	0.02
Colder et al. <sup>36</sup>	7	410	30	0.08
Park et al. <sup>37</sup>	Not reported	450	65	* 0.18

# 6. Summary and conclusions

This research focuses on the effects of precipitation on the thermal conductivity of Ni-doped ZnO. The goals of this study are manipulating thermal conductivity by controlling nucleation and growth of NiO-precipitates, thereby enhancing the TE conversion efficiency, and drawing the correlation between thermal conductivity variations and microstructure evolution. We prepared pure ZnO and super-saturated Ni-doped ZnO samples by sintering at 1400 °C followed by air-quenching. NiOprecipitates were formed by heat treatments at 750, 800, and 900 °C for different durations. We characterized the materials using XRD and HRSEM, and analyzed the micrographs to evaluate microstructural features such as grain size, precipitate number density, average radius and volume fraction, and their temporal evolution. Seebeck coefficient and thermal and electrical conductivities were measured at temperatures between 50 to 700 °C. Our main findings can be summarized as follows:

- 1. Interplay between precipitate and solid-solution scattering mechanisms was introduced for this system. We observed slight reduction of thermal conductivity for the sample aged at 750 °C for 8 and 16 h, compared to asquenched samples. Based on comparison between experimental and calculated thermal conductivity, this trend is associated to the relatively high precipitate number density of these samples.
- The solid-solution effect is often comparable with U-processes, and is found to be a significant phonon scattering mechanism that competes the precipitate scattering mechanism.
- 3. A minimum thermal conductivity as low as 8.0  $W \cdot m^{-1} K^{-1}$  was obtained in this study at 700 °C for the samples aged at 750 °C for 8 h.
- 4. The as-quenched samples exhibit the highest electrical conductivity, with values as high as  $17.9 \text{ S} \cdot \text{cm}^{-1}$  at 700 °C. Aging at 750 °C results in decrease of the electrical conductivity values with time due to depletion of Ni-solute atoms from the matrix, which act as electron donors. Accordingly, the pure ZnO specimens exhibit the lowest electrical conductivity values for the entire temperature range.
- 5. The pure ZnO samples show the highest Seebeck coefficient absolute value as high as 517  $\mu$ V·K<sup>-1</sup> at 700 °C, whereas the as-quenched samples exhibit the lowest absolute value of 308  $\mu$ V·K<sup>-1</sup> at this temperature. Similarly to the electrical conductivity, the Seebeck coefficient is affected by the dissolved Ni-atoms in the ZnO-matrix as well.
- The as-quenched samples exhibit the highest ZT-values, as high as 0.02 at 700 °C.
- 7. The  $\kappa_e$ -values evaluated for the pure ZnO, as-quenched, and the samples aged at 750 °C, are found to be lower than the respective  $\kappa_p$ -values by a few orders of magnitudes. The  $\kappa_p$ -values decrease with increasing temperature due to phonon scattering in U-processes, whereas the  $\kappa_e$ -values exhibit the opposite trend, indicative of a non-degenerate semiconducting behavior.
- 8. Classical trends of microstructure evolution for aged samples were observed. The precipitate number density increases and their average radius decreases with decreasing aging temperature. The maximum number density value obtained in this study is  $1.6 \cdot 10^{20}$  m<sup>-3</sup> for the samples aged at 750 °C for 48 h.

### 7. Recommendations for further research

Following this study, there are several questions that remain open, and should be addressed. On the technological aspect:

- 1. Electrical measurements should be performed for the thermally aged samples at 800 and 900 °C.
- 2. Further aging temperatures should be tested to maximize the precipitate number density value, while the precipitate volume fraction should be kept as small as possible.
- 3. Improvement of the powder pressing process for the bar-shaped specimens should be performed to obtain a higher green-body density, which should further lead to higher final density and better electrical conductivity.
- 4. Using of a nanometric size raw material powder or applying a milling process should be performed to achieve grain refinement and consequently reduction of material's thermal conductivity.
- 5. The microstructure stability of the samples as a function of aging time and temperature should be evaluated.

On the scientific level, the following questions should be addressed:

- Evaluation of the precipitate number density in this study is performed by analyzing SEM micrographs under several assumptions. Using advanced methods such as transmission electron microscopy (TEM) and atom probe tomography (APT) would provide more reliable results for the high number density regime.
- 2. The evaluated NiO-precipitate volume fraction in this study is used as an input for the Callaway model for the solid-solution scattering mechanism. This mechanism was found out to be predominating in Ni-doped ZnO system. However, currently it is determined with poor accuracy by analyzing SEM micrographs. Therefore, the solute Ni-atom concentration in the ZnO-matrix should be determined directly and more accurately by applying X-ray

diffraction (XRD). This method is highly sensitive to variation of lattice parameters, as a result of solid-solution effect. Wavelength dispersive x-ray spectroscopy (WDS) analysis can also be helpful for this purpose.

- 3. To further understand the role of the solid-solution scattering mechanism,  $\tau_{PD}^{-1}$ , in Ni-doped ZnO system the approach that performed by Gelbstein et al. <sup>70, 71</sup> can be applied. By using this approach, the dependence of the lattice thermal conductivity on dopant concentration in a single-phase solid-solution can be calculated. Preforming this calculation in our study may provide the optimum Ni-doping level in ZnO-matrix, which yields minimum values of lattice thermal conductivity for the system.
- Studying NiO-precipitate growth orientation should be considered and can be performed by applying electron backscatter diffraction (EBSD) analysis or TEM.
- 5. The Ni-doped ZnO electronic properties vary significantly due to changes in the dissolved Ni-atoms in the ZnO-matrix. Further investigations applying theoretical and computational approaches are needed to correlate between these changes to the microstructure temporal evolution.
- 6. Co-doping with an additional element should also be considered. Each of the dopants will have different purpose. The first will be used as precipitation-forming, while the second one will remain in the ZnO-matrix and used for tailoring the electrical properties of the matrix.

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# השפעת התבדלות על המוליכות התרמית של תחמוצת אבץ תרמואלקטרית מאולחת

עידו כורש

## השפעת התבדלות על המוליכות התרמית של תחמוצת אבץ תרמואלקטרית מאולחת

חיבור על מחקר

## לשם מילוי חלקי של הדרישות לקבלת תואר מגיסטר למדעים במדע והנדסה של חומרים

### עידו כורש

הוגש לסנאט הטכניון – מכון טכנולוגי לישראל

2017 שבט תשע"ז, חיפה, פברואר שבט

### תודות:

המחקר נעשה בהנחייתו של פרופ"מ ירון אמויאל בפקולטה למדע והנדסה של חומרים בטכניון – מכון טכנולוגי לישראל.

אני רוצה להודות למשפחתי, במיוחד לאישתי שמרית, על התמיכה הרבה לאורך כל תקופת הלימודים. בנוסף, ברצוני להודות לפרופ"מ ירון אמויאל על הנחיותו המעמיקה והעושר המדעי שקיבלתי לאורך כל תקופת המחקר. תודה נוספת היא לחברי קבוצת החומרים התרמואלקטריים ובמיוחד לגל בכר אשר סייעה לי רבות במדידות תכונות תרמואלקטריות.

### תקציר:

חומרים תרמואלקטריים ממירים אנרגיה תרמית לאנרגיה חשמלית, ולהפך. פעילות קבוצת חומרים זו מבוססת על אפקט Seebeck אשר התגלה ב-1821. לפי אפקט זה, כאשר מחממים צומת בין שני חומרים שונים נוצר מתח חשמלי בצומת בצד בו אינם מחוברים. החומרים התרמואלקטריים משמשים ליישומים של המרת אנרגיה, החלפת חום וקירור.

(ZT) מאפיין מרכזי המגדיר את איכות החומרים התרמואלקטריים הינו "גורם הטיב" התרמואלקטרי (ZT). מאפיין מרכזי המגדיר את איכות החומרים של החומר: מקדם S, Seebeck, מוליכות חשמלית,  $\sigma$ , מוליכות חשמלית,  $\sigma$ , גבוה יותר עבור חומר מסוים, כך הנצילות התרמודינמית המרבית ומוליכות תרמית,  $\pi$ . ככל ש-ZT גבוה יותר עבור חומר מסוים, כך הנצילות התרמודינמית המרבית הנמוליכות תרמית, המנו כחומר תרמואלקטרי גבוהה יותר. הגדלת ZT ניתנת להשגה ע"י בחירת חומר בעל הניתנת להפקה ממנו כחומר תרמואלקטרי גבוהה ומוליכות תרמית נמוכה. האתגר בדרישה זו טמון בקשר מקדם Seebeck גבוה, מוליכות חשמלית גבוהה ומוליכות תרמית נמוכה. האתגר בדרישה זו טמון בקשר הקיים בין שלושת מאפיינים אלו בחומר ותלותם בריכוז נושאי המטען. לדוגמא, עליה בריכוז נושאי המטען גוררת עליה במוליכות החשמלית של החומר, אך מנגד מביאה לירידה בערכו של מקדם המטען גוררת עליה במוליכות החשמלית של החומר, אך מנגד מביאה לירידה בערכו של מקדם Seebeck המטען גוררת עליה במוליכות החשמלית נובעת מהקשר בין מוליכות חשמלית למוליכות התרמית בחומר. המטען התלוי בחומר. המוזכר לעיל, נובעת מהקשר בין מוליכות חשמלית למוליכות התרמית למוליכות התרמית בחומר. הנונים בין מוליכות התרמית למוליכות התרמית מורכבת משני רכיבים: רכיב שריגי (פונוני) ורכיב של נושאי המטען התלוי בין השאר בריכוזם. עליה בריכוז נושאי המטען תניב עליה במוליכות החשמלית, אך עם זאת תגרום גם לעליה לא רצוייה במוליכות התרמית.

טיב החומר התרמואלקרטי רגיש במיוחד למאפייני המיקרומבנה שלו, על-כן הנדסה ושינוי המיקרומבנה של החומר מאפשרת שליטה בתכונות התרמואלקטריות שלו וביעילותו. אחד החומרים התרמואלקטריים המבטיחים הינו תחמוצת האבץ (ZnO). חומר זה משלב בין יעילות תרמואלקטרית סבירה, עמידות בסביבה כימית קיצונית וטמפרטורות גבוהות, ועלות נמוכה יחסית.

מחקר זה מתמקד בהשפעת התבדלות על ההולכה התרמית של ZnO מאולח בניקל (Ni) עבור יישומים תרמואלקטריים. יצירת מתבדלים בריכוז גבוה חיונית לפיזור פונונים בחומר, וגוררת הורדת ההולכה התרמית שלו ושיפור גורם הטיב התרמואלקטרי (ZT). במסגרת המחקר הוכנה תמיסה רווית-יתר בריכוז 3% אטומי של Ni ב-ZnO ע"י סנטור ב-1400 מ"צ, המסתיים בחיסום לטמפרטורת החדר. יצירה וגידול של מתבדלים של תחמוצת ניקל (NiO) בגודל ננומטרי עד תת-מיקרוני בצורה מבוקרת בוצעה ע"י טיפולים תרמיים (זיקון) בשלוש טמפרטורות: 750, 800 ו-900 מ"צ ובתחום זמנים של 2 עד 48 שעות.

התפתחות המיקרומבנה כתלות בזמני הזיקון נחקרה. תכונות המיקרומבנה כמו: גודל גרעין, ריכוז מתבדלים, רדיוס ממוצע והשבר הנפחי שלהם אופיינו ע"י מיקרוסקופ אלקטרונים. ההולכה התרמית של הדגמים נקבעה ע"י שיטת (LFA) מ-50 מ"צ ועד 700 מ"צ, בנוסף הולכה

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חשמלית ומקדם סיבק נמדדו גם הם בטווח טמפרטורות זה. נצפתה ירידה בהולכה התרמית ב-50 מ"צ מ-חשמלית ומקדם סיבק נמדדו גם הם בטווח טמפרטורות זה. נצפתה ירידה בהולכה התרמית ב-50 מ"צ מים אישר 17.6 W·m<sup>-1</sup>K<sup>-1</sup> ו-17.4 W·m<sup>-1</sup>K<sup>-1</sup> עבור הדגמים המחוסמים עד ל 17.4 W·m<sup>-1</sup>K<sup>-1</sup> ו-17.4 W·m<sup>-1</sup>K<sup>-1</sup> עבור הדגמים המחוסמים שזוקנו ב- 750 מ"צ למשך 16 שעות. לעומת זאת, שווקנו ב- 750 מ"צ למשך 16 שעות. לעומת זאת, עבור דגמים אלו, לדוגמא 1.6·10<sup>20</sup> m<sup>-3</sup> 1.6·10<sup>20</sup> m<sup>-3</sup> עבור דגמים אלו, לדוגמא 1.6·10<sup>20</sup> m<sup>-3</sup> אשר זוקנו ב- 750 מ"צ למשך 16 שעות. לעומת זאת, עבור דגמים אלו, לדוגמא 50·10<sup>20</sup> m<sup>-3</sup> ליכיח השמלית מ-100 מ"צ למשך 16 שעות. לעומת זאת, יצירה וגידול של המתבדלים הובילו לירידה בהולכה החשמלית מ-10<sup>-1</sup> S·cm<sup>-1</sup> עבור הדגמים המחוסמים יצירה וידידה של המתבדלים הובילו לירידה בהולכה מ"צ למשך 18 ו-24 שעות, בהתאמה. מגמה שונה ל-3.0 ו-2.2 מ"צ למשך 18 ו-24 שעות, בהתאמה. מגמה שונה התקבלה עבור מקדם סיבק: הדגמים המחוסמים ואלו המזוקנים ב-750 מ"צ למשך 18 ו-24 שעות הציגו התקבלה עבור מקדם סיבק: הדגמים המחוסמים ואלו המזוקנים ב-750 מ"צ למשך 18 ו-24 שעות הציגו התקבלה עבור מקדם סיבק: הדגמים המחוסמים ואלו המזוקנים ב-750 מ"צ למשך 18 ו-25 שעות הציגו התקבלה עבור מקדם סיבק: הדגמים המחוסמים ואלו המזוקנים ב-750 מ"צ למשך 18 ו-25 שעות הובילו לירידה ב-27 מ"צ התקבל עבור הדגמים המחוסמים. בוצע דיון על אירידה ב-27, כאשר ערך מירבי של 10.0 ב-700 מ"צ התקבל עבור הדגמים המחוסמים. בוצע דיון על הולכה השפעת הגורמים השונים במיקרומבנה של החומר כמו: מתבדלים, זיהומים וגבולות גרעין על הולכה השמלית ותרמית, ולבסוף הוצג הקשר בין התפתחות מיקרומבנה החומר לתכונות אלו של מוס.