Sintering characteristics and thermoelectric properties of Mn–Al co-doped ZnO ceramics

Joshua HOEMKE,† Atta Ullah KHAN,* Hidehiro YOSHIDA,** Takao MORI,* Eita TOCHIGI,* Naoya SHIBATA, Yuichi IKUHARA and Yoshio SAKKA**

Institute of Engineering Innovation, The University of Tokyo, 2–11–16 Yayoi, Bunkyo-ku, Tokyo 113–8656, Japan
†National Institute of Materials Science (NIMS), 1–1 Namiki, Tsukuba 305–0044, Japan
**National Institute of Materials Science (NIMS), 1–2–1 Sengen, Tsukuba 305–0047, Japan

Polycrystalline Mn–Al co-doped ZnO ceramics were prepared by sintering in air. Increasing Mn dopant concentration led to an increase of the ZnO lattice constants indicating substitution of Mn on the Zn sublattice. A Mn-rich spinel secondary phase was also detected within grains and at grain boundaries. The addition of Al dopant led to an initial reduction in grain size while the addition of Mn led to an increase in grain size. Thermoelectric property measurements revealed that Al doping led to a large initial increase in electrical conductivity and increasing Mn dopant addition resulted in electrical conductivity reduction. The absolute value of the Seebeck coefficient was largely unaffected at low Mn doping levels; however, an increase was observed for high Mn doping levels. The thermal conductivity showed a marked decrease with increasing Mn concentration, indicating the effectiveness of Mn dopant substitution for Zn to reduce the thermal conductivity by point defect scattering. Overall, the maximum ZT was achieved for the Zn0.99Al0.01O sample (ZT = 0.35 at 1273 K and ZT = 0.44 at 1000 K). By doping or changing stoichiometry it has proven possible to increase the ZT of select oxides to near practical efficiency. Nevertheless, challenges such as the question of stability of Na2CoO4 at high temperature due to the volatility of Na as well as the lack of an n-type oxide thermoelectric with a ZT near 1 remain and the investigation of new thermoelectric oxide material systems is crucial for overcoming them and improving the prospects for practical applications of oxide thermoelectrics.

ZnO has shown potential for thermoelectric applications due to its low cost, nontoxicity and stability to high operating temperatures of >1273 K in air. However, despite the large power factors, PF, where PF = S2T/κ, that have been achieved [i.e. PF = 23 × 10–2 W/(m·K2) at 1273 K in Al–Ga co-doped ZnO], the high thermal conductivity of ZnO remains a drawback to improving the ZT of ZnO further. Previous studies have attempted to reduce the thermal conductivity by reducing grain size and by introducing point defects to scatter short wavelength phonons. However, grain size reduction can have the adverse effect of electrical conductivity reduction and solid solution alloying can result in electrical conductivity reduction due to the electronegativity mismatch of the matrix element and substitutional dopant, resulting in diminution instead of improvement of the ZT.

In this study, polycrystalline samples of Mn–Al co-doped ZnO have been produced in order to study the effect of co-doping on microstructural and thermoelectric properties with the aim of improving thermoelectric performance. Al is known to act as a donor and can improve the electrical conductivity of ZnO by up to 3 orders of magnitude. Mn has a high solubility (~8 at% at 1400°C) in ZnO and can act as a point defect to reduce thermal conductivity. First principles calculations also show that Mn has a tendency for clustering in ZnO and spinodal decomposition has been suggested to occur in Mn–Al co-doped ZnO.
The presence of nanoscale phase-separated Mn-rich regions or spinodal decomposition could result in an additional decrease of the thermal conductivity. In addition, in contrast to previous studies where co-doping of Mg and Al was attempted to improve the ZT of ZnO, the Mn dopant which has an electronegativity close to that of Zn has been studied. The small electronegativity difference could result in reduced electrical conductivity diminution due to alloy scattering compared to Mg and Al co-doping and this, combined with thermal conductivity reduction, could result in increased ZT values.

2. Methods

2.1 Sample preparation

Ceramic powder mixtures were produced by first weighing ZnO (Nanotek, 99.9% purity, 34 nm), Mn3O4 (Nanotek, 99.5% purity, 56 nm) and Al2O3 (Taimicron TM-DAR, 99.99% purity, 100 nm) in appropriate ratios to produce samples of Zn1-xAlxO. Additional high resolution data for identifying secondary phase peaks near 2θ = 31.23 and 36.8° was collected by X-ray diffraction (Smartart, Rigaku, 40 kV, 30 mA) using Cu-Kα radiation over a 2θ range of 20°–38° and using a scan speed of 0.2°/min and scan step of 0.01°. Microstructure characterization was done using a JEOL 6510 (La) scanning electron microscope (SEM) operating at 15 kV with energy dispersive spectroscopy (EDS) elemental analysis capability. Grain size was measured from SEM images using the line intercept method.

2.2 Characterization

2.2.1 Phase and microstructure analysis

Samples for microstructure and phase analysis were prepared by first polishing the sintered pellets using 9, 3, 1 and 0.5 μm diamond slurry to obtain a mirror surface and then etching the samples at 1300 or 1350°C for 30 min. Phase analysis of the sintered polycrystals was carried out by X-ray diffraction (XRD, Ultima III X-ray diffractometer, Rigaku, 40 kV, 40 mA) using Cu-Kα radiation over a 2θ range of 25–70° with a scan speed of 1.2°/min and scan step of 0.02°. Microstructure characterization was done using a JEOL 6510 (La) scanning electron microscope (SEM) operating at 15 kV with energy dispersive spectroscopy (EDS) elemental analysis capability. Grain size was measured from SEM images using the line intercept method.

3. Results and discussion

3.1 Phase analysis and microstructure characterization

The XRD profile for the Zn1−xAlxO ceramics is shown in Fig. 1. The primary phase peaks are indexed according to the ZnO wurtzite structure. (b) (top) XRD data for the ZnO (103) peak showing the peak shift with Mn doping. (bottom) XRD data for 2θ = 30°–38° with spinel peaks indicated by labels. Additional minor peaks near 2θ = 31 and 32.6° are due to Cu-Kα diffraction from the ZnO (002) and (101) peaks respectively.

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For electrical transport measurements a bar-shaped sample was prepared by cutting using a diamond isometric cutter and then polishing the sides to obtain a typical cross section of ~2 × 3 mm² with a typical sample length of 8–11 mm. The resistivity and Seebeck coefficient were measured from 50°C to 730°C using the ZEM-2 (Ulvac Riko) which measures both properties simultaneously. The resistivity is measured using the four-probe method. For Seebeck coefficient measurement a temperature difference ΔT of 10, 20 and 30 K was applied at each temperature and the Seebeck coefficient was determined from the ΔV/ΔT plot. The thermal conductivity was determined from the expression: $\kappa = \alpha C_p \rho$, where $\kappa$ is thermal diffusivity, $C_p$ is specific heat and $\rho$ is density. The thermal diffusivity was measured from room temperature (RT) to 750°C using the laser flash method (Ulvac Riko, TC-7000). For the laser flash method a pellet sample of typical diameter and thickness of 10–11 and 1–2 mm respectively is used. A black carbon spray coating is applied to reduce measurement errors due to thermal emissivity losses. The $C_p$ values were determined using literature values for pure ZnO. Resistivity and Seebeck coefficient measurements were made perpendicular to the pressing direction and thermal diffusivity measurements were made parallel to the pressing direction of the pellet. The density was determined either by Archimedes’ method or by using sample weight and dimensions.

The ZnO wurtzite phase (space group $\text{P6}_3\text{mc}$) has the following unit cell parameters: $a = b = 3.2495$ Å and $c = 5.2067$ Å. The X-ray diffraction (XRD) pattern for the Zn1−xAlxO samples is shown in Fig. 1. Major peaks belonging to the ZnO wurtzite phase (space group $\text{P6}_3\text{mc}$) have been indexed.

3.2 Laser flash measurements

In addition to the four-probe method, the resistivity and Seebeck coefficient were measured using a laser flash method (Ulvac Riko, TC-7000). For the laser flash method a pellet sample of typical diameter and thickness of 10–11 and 1–2 mm respectively is used. A black carbon spray coating is applied to reduce measurement errors due to thermal emissivity losses. The $C_p$ values were determined using literature values for pure ZnO. Resistivity and Seebeck coefficient measurements were made perpendicular to the pressing direction and thermal diffusivity measurements were made parallel to the pressing direction of the pellet. The density was determined either by Archimedes’ method or by using sample weight and dimensions.

The presence of nanoscale phase-separated Mn-rich regions or spinodal decomposition could result in an additional decrease of the thermal conductivity. In addition, in contrast to previous studies where co-doping of Mg and Al was attempted to improve the ZT of ZnO, the Mn dopant which has an electronegativity close to that of Zn has been studied. The small electronegativity difference could result in reduced electrical conductivity diminution due to alloy scattering compared to Mg and Al co-doping and this, combined with thermal conductivity reduction, could result in increased ZT values.
doped ZnO have previously been reported to follow Vegard’s law. Mn has substituted at the Zn site. The lattice parameters of Mn-doped samples are labeled in Fig. 1(a). With increasing Mn dopant concentration the peak location for the ZnO phase shifted to lower 2θ values. The change of the lattice constants, a and c (Å), with Mn dopant concentration is shown in Fig. 2. There is a trend of increasing lattice constant values with increasing Mn doping level, indicating that Mn has substituted for Zn in the ZnO lattice. This is consistent with previous reports where Mn is reported to have a solubility of ~8 at% in ZnO at 1400°C. Peak locations for the ZnO wurtzite phase were observed to shift to lower 2θ values as shown for the (103) peak in Fig. 1(b) (top). This can be attributed to the larger cation radius of the Mn2+ cation compared to the Zn2+ cation. A similar shift with increasing Mn doping level indicates that Mn enters the spinel lattice, replacing Zn, and produces a phase with a Zn1-xMnxAl2O4 composition. The change in lattice parameter for increasing Mn concentration to 5 at% Mn from the theoretical prediction indicates that Mn has substituted at the Zn site. The lattice parameters of Mn-doped ZnO have previously been reported to follow Vegard’s law. Minor peaks can also be identified at 2θ = 31.23 and 36.8° in Fig. 1(b) (bottom) for the Zn0.99Al0.01O sample. These peaks are consistent with the (220) and (311) peaks of the gahnite spinel phase, ZnAl2O4 (space group 227,Fd-3m, ICDD card #01-070-8181) which may be formed by a reaction between ZnO and Al2O3. The (220) and (311) peaks in Fig. 3 are also shown. The c lattice parameter follows the theoretical prediction of Vegard’s law closely, with a deviation of only ~1 at% Mn. The deviation of the a lattice parameter is slightly larger but still only deviates by several at% Mn from the theoretical prediction. The close agreement of the experimental a and c values with those predicted by Vegard’s law closely, with a deviation of only 0.2%, indicates that Mn has substituted for Zn in the ZnO lattice. This is consistent with previous reports where high densities (near theoretical density) have been achieved for ZnO sintered at 1300–1400°C with a theoretical density of 5.67 g/cm³ for ZnO and 5.412 g/cm³ for MnO. The high theoretical density achieved for the Zn0.99Al0.01O sample is consistent with previous reports where high densities (near theoretical density) have been achieved for ZnO sintered at 1300–1400°C with a theoretical density of 5.67 g/cm³ for ZnO.
The presence of peaks belonging to a Mn-rich Zn matrix, Al and O and depleted of Zn. This is consistent with As shown in Fig. 4, EDS analysis showed these precipitates to be MnAl₂O₄ phase, consistent with the microstructure detected by EDS analysis. In addition, both Al and Mn were detected in the ZnO matrix by EDS analysis indicating the solubility of these cations in the ZnO lattice. The reason for the difference in grain size for Al-doped and Al–Mn co-doped ZnO samples may be due to differences in the sintering mechanism of ZnO due to the Al and Mn dopants. Zener pinning, in which grain growth is retarded due to the presence of fine precipitates has been suggested as the cause for the reduced grain growth in Al-doped ZnO ceramics.²⁴,²⁷ The increased grain size observed in Mn–Al co-doped samples can be attributed to the increased mass transfer that may occur at grain boundaries in Mn-doped ZnO.²⁶ The Mn dopant can segregate to the ZnO grain boundary to some extent and creates either defects, a secondary phase or an amorphous film, which can enhance the diffusion occurring at grain boundaries. Although Mn–Al co-doped samples also contain spinel precipitates which may affect grain growth by a pinning mechanism, it is this enhanced mass diffusion due to the Mn dopant that may lead to the increased grain size observed in the Mn–Al co-doped samples. At high Mn doping levels (10 at%) a pronounced change in the microstructure was observed. As shown in Figs. 4(d) and 6, due to the high Mn doping amount, segregation of Mn at the grain boundaries with a corresponding depletion of Zn occurred. For low doping levels of Mn, during cooling some of the Mn dopant may come out of solution and form a Zn₁₋ₓMnₓAl₂O₄ phase, possibly by reacting with the ZnAl₂O₄ phase that can be formed at a lower temperature of 800–1000°C.²⁴ It is possible that in this process the Mn replaces Zn in the spinel structure, resulting in the Mn-rich, Zn-depleted spinel phase detected by EDS. This is further supported by the shift to lower 2θ values of the peaks belonging to the spinel impurity phase. At high Mn concentrations, i.e. 10 at% Mn doping level, even at high temperature (1400°C) the Mn concentration in ZnO is already saturated and the excess Mn could segregate at the grain boundaries or react to form Mn-rich spinel precipitates, consistent with the microstructure detected by EDS analysis.

### 3.2 Thermoelectric properties

#### 3.2.1 Electronic transport

The electrical resistivity and Seebeck coefficient measured for ZnO doped with 0, 1, 2, 5 and 10 at% Mn and 1 at% Al are shown in Figs. 7(a) and 7(b) respectively. The resistivity value of Zn₀.₉₉Al₀.₀₁O at 50°C is comparable to previous reports for Al-doped ZnO.¹² With increasing Mn concentration the resistivity increases. For 10 at% Mn doping, the temperature dependence

| Sample | Density (g/cm³) | Theor. Dens. (%) | Avg. Grain Size (μm) | Precipitate Size (μm) |
|--------|----------------|-----------------|---------------------|--------------------|
| Zn₀.₉₉Al₀.₀₁O | 5.66 | 99.8 | 12.7 | 0.39 |
| Zn₀.₉₉Mn₀.₀₁Al₀.₀₁O | 5.46 | 96.3 | — | — |
| Zn₀.₉₉Mn₀.₀₂Al₀.₀₁O | 5.24 | 92.4 | 22.8 | 0.95 |
| Zn₀.₉₉Mn₀.₀₂Mn₀.₀₁O | 5.33 | 94.0 | 22.8 | 1.7 |
| Zn₀.₉₉Mn₀.₀₁Al₀.₀₁O | 5.28 | 93.1 | — | — |

**Table 1.** Measured density and avg. grain size

**Fig. 4.** SEM images showing the microstructure of (a) 1 at% Al-doped ZnO (b) 2 at% Mn – 1 at% Al-doped ZnO (c) 5 at% Mn – 1 at% Al-doped ZnO and (d) 10 at% Mn – 1 at% Al-doped ZnO sintered in air at 1400°C for 12 hr.

**Fig. 5.** Elemental mapping obtained by EDS for the 5 at% Mn – 1 at% Al-doped ZnO sample. Mn, Al, and O-rich and Zn-poor precipitates are present within grains and at grain boundaries.
of the resistivity changes to show behavior characteristic of a semiconductor with activated electrical conductivity. For low Mn doping levels there is a gradual shift of resistivity behavior from metallic to semiconducting with increasing Mn concentration. The Zn$_{0.99}$Al$_{0.01}$O sample shows a fully metallic behavior and the Zn$_{0.97}$Mn$_{0.02}$Al$_{0.01}$O sample has a transition from metallic to semiconducting character near 600°C. The Zn$_{0.94}$Mn$_{0.05}$Al$_{0.01}$O sample shows a semiconducting behavior over the entire temperature range. This shift in behavior could be due to the increasing formation of Mn deep acceptor levels which could lower the Fermi level and reduce the number of donor and shallow acceptor levels\textsuperscript{28,29} resulting in a shift from metallic or degenerate semiconductor character to that of a semiconductor with activated conductivity.

The increasing barrier to electron transport resulting from increasing Mn dopant concentration could be attributed to a combination of the high concentration of a secondary phase, i.e. the Zn$_{1-x}$Mn$_x$Al$_2$O$_4$ phase, which can scatter electrons, the high concentration of Mn ions substituting for Zn and leading to alloy scattering, a high density of Mn impurities creating impurity levels within the band gap (Mn is known to produce deep acceptor levels\textsuperscript{29}) and also the increase of the barrier height to electron transport at the grain boundary. SEM-EDS analysis shows the segregation of Mn to the grain boundary. Similar to Mn, Co has been shown to segregate to the grain boundaries of ZnO.\textsuperscript{30} The segregation of Co has been shown to increase the varistor nonlinearity, possibly due to the increase of acceptor-type defects at the grain boundary.\textsuperscript{31} An increase in these defects can increase the n-p-n barrier height at the grain-grain boundary interface and lead to an increased barrier to electron transport.

The Seebeck coefficient for 0, 1, 2, 5 and 10 at% Mn – 1 at% Al-doped ZnO samples is shown in Fig. 7(b). The negative values indicate that the material is n-type. This can be due to the Al dopant acting as a donor to produce electrons according to the following expression:\textsuperscript{32}

$$\text{Al}_2\text{O}_3 \rightarrow 2\text{Al} + 2\text{e}^- + 2\text{O}_2 + \frac{1}{2}\text{O}_2.$$  \(\text{(1)}\)

and also can be due to oxygen vacancies produced during high temperature sintering which can act as donors and produce additional electrons. With increasing temperature, the point defect concentration will increase according to the equation:\textsuperscript{33}

$$c = N_{\text{sites}} \exp \left( - \frac{E'}{k_B T} \right),$$  \(\text{(2)}\)

where \(c\) is the point defect concentration, \(N_{\text{sites}}\) is the number of sites available for defect formation, \(E'\) is the defect formation energy, \(k_B\) is the Boltzmann constant and \(T\) is temperature. With increasing temperature the concentration of oxygen vacancies will rise and can make a contribution to increasing the overall electrical conductivity.
The absolute value of the Seebeck coefficient also shows the conventional character of increasing in absolute value with increasing resistivity. However, the Seebeck coefficient shows little variation at low Mn doping level (up to 5 at% Mn). Thus it is likely that the Mn dopant acts as a neutral impurity in the Mn$^{2+}$ state and does not affect the Seebeck coefficient which for a metal or degenerate semiconductor can be expressed as:

$$S = \frac{2e\tau_p^0}{\hbar} \frac{v_F}{\hbar} \left( \frac{\pi}{3n} \right)^{1/3},$$

(3)

where $e$ is the electron charge, $\hbar$ is the Planck constant, $m^*$ is the electron effective mass, and $n$ is the carrier concentration. The Seebeck coefficient is largely unchanged for low Mn doping (<5 at%), indicating that the carrier concentration is not strongly affected by the increasing Mn doping level.

The electrical conductivity, $\sigma$, can be described by the expression: $\sigma = ne\mu$, where $\mu$ represents the mobility. The increasing resistivity observed for low Mn doping levels is likely due to a decrease of mobility and may not be caused by a carrier concentration variation. The increasing level of Mn impurities creates point defects in the ZnO lattice. These impurities may reduce the mobility by alloy scattering of electrons. The presence of the spinel precipitates can also increase electron scattering and contribute to the increase in resistivity. At the highest Mn doping level (10 at%), the Seebeck coefficient shows a large increase in absolute value with a significant increase relative to other samples with low Mn dopant concentration beginning near 400°C. This increase may be due to the high volume concentration of the secondary spinel phase (ZnAl$_2$O$_4$ is known to be a wide-bandgap semiconductor with a band gap that may be as large as 6.55 eV),$^{35}$ the significant segregation of Mn at grain boundaries, which could create a potential barrier to selectively scatter low energy carriers and increase the Seebeck coefficient$^{36}$ or the large number of Mn impurities which can create deep acceptor levels within the band gap, resulting in enhancement of the Seebeck coefficient.$^{37}$

The power factor is shown in Fig. 7(c). The power factor increases with temperature and a maximum value of 6.57 $\times$ 10$^{-4}$ W/(m·K) is attained at 730°C for the 1 at% Al-doped sample. This value is comparable with previous literature values for Al-doped ZnO samples sintered in air.$^{14}$ With increasing Mn dopant amount the power factor begins to decrease, due to the increase of the electrical resistivity.

### 3.2.2 Thermal transport

The thermal conductivity values of 0, 1, 2, 5 and 10 at% Mn – 1 at% Al co-doped ZnO samples are shown in Fig. 8(a). The 0 at% Mn – 1 at% Al doped ZnO sample shows the highest values and the thermal conductivity drops with increasing Mn dopant concentration. At low temperature the effect is significant, with ~40% decrease for 2 at% Mn doping compared to the undoped sample at RT.

The thermal conductivity can be described generally by the expression:$^{38}$

$$\kappa = \frac{k_B}{2\pi^2 v_F} \left( \frac{k_B T}{h} \right)^3 \int_0^{\infty} \tau_{c}(x) \frac{x^4 e^{-x}}{(e^x - 1)^2} \, dx,$$

(4)

where $v_F$ is the speed of sound, $h$ is the reduced Planck constant, $\theta$ is the Debye temperature, $\tau_{c}$ is the total relaxation time for phonon scattering processes and $x = \omega a/(k_B T)$, where $\omega$ is the phonon frequency. The relaxation time can be written as a function of several terms:$^{39}$

$$\tau_{c}^{-1} = \tau_{p}^{-1} + \tau_{D}^{-1} + \tau_{B}^{-1},$$

(5)

where $\tau_{p}^{-1}$, $\tau_{D}^{-1}$, and $\tau_{B}^{-1}$ are the relaxation time due to phonon-phonon scattering processes, defect scattering and boundary scattering respectively. For a semiconductor doped with a high concentration of impurities the defect scattering term will become significant. Generally, this term has the form: $\tau_{\text{def}}^{-1} = A \cdot a^{\alpha}$, where $A$ is defined as the defect scattering coefficient, which is given by the expression: $A = \xi_0 \cdot \Gamma / (4\pi \xi^3)$. Here, $\xi_0$ is the unit cell volume and $\Gamma$ is the scattering parameter, which is used to describe the strength of a point defect to scatter phonons. Generally, $\Gamma$ is written as:$^{39}$

$$\Gamma_1 = \xi_0 \left[ \left( \frac{M_f - M}{M} \right)^2 + \frac{\delta}{\delta} \frac{\delta}{\delta} \right],$$

(6)

where $\xi_0$ is the impurity concentration, $M_f$ the defect mass, $M$ the average mass of atoms in the solid, $\delta$ a parameter describing size mismatch, $\delta$ the atomic size of the defect, and $\overline{\delta}$ the average size of atoms in the solid. The expression for $\Gamma$ due to Mn doping on the Zn site can be written as:$^{39}$

$$\Gamma = \frac{1}{2} \left[ \frac{M_{\text{Mn}} - M_{\text{Zn}}}{M} \right]^2,$$

(7)

where $M_{\text{Mn}}$ is the mass of the Mn dopant and $M_{\text{Zn}}$ is the average mass on the Zn site. Thus, the scattering due to point defect substitution will be linearly proportional to the dopant concentration and proportional to the square of the mass mismatch of the defects.

A plot of $\kappa$ and $\Gamma$ values is shown in Fig. 8(b). Here, increasing $\Gamma$ corresponds to increasing Mn concentration (for 0, 1, 2, 5 and 10 at% Mn – 1 at% Al doping levels). $\Gamma$ is determined using Eq. (7), accounting for the mass contrast between Mn and Zn, with a similar additional term for the Al dopant and Zn mass.
contrast added. The term for strain in Eq. (6) is not included because the $\varepsilon$ and $\delta$ parameters are not known. The solubility of Al in ZnO has been determined to be $\sim0.3$ at%. Thus this value is included for all samples. For the 10 at% Mn-doped ZnO sample, a value of 8 at% Mn is used because this is near the solubility limit of Mn at 1400°C in ZnO.\(^{(13)}\)

As expected, an inverse relationship between $\kappa$ and $\Gamma$ is obtained, indicating the effectiveness of Mn dopant substitution for reducing $\kappa$ by point-defect scattering. Since Mn$^{2+}$ and Zn$^{2+}$ have $\sim16\%$ difference in atomic mass and the solubility of Mn is approximately 8 at% at 1400°C, the Mn dopant can effectively act as a point defect to reduce the thermal conductivity of ZnO by short wavelength phonon scattering. The increase of the ZnO lattice parameters and the agreement with Vegard’s law further supports the substitution of Mn for Zn. Indeed, a strong reduction of the thermal conductivity is observed near RT for the Mn doped samples; however, with increasing temperature this effect is diminished due to the increasing strength of the $\tau_p^{-1}$ term, representing the increasing dominance of phonon-phonon scattering processes at high temperature. Point defect scattering due to Mn substitution for Zn appears to account for the reduction in the thermal conductivity and an additional mechanism resulting in strong thermal conductivity reduction such as nanoprecipitate formation or spinodal decomposition is not observed. However, the presence of Mn-rich regions at the nanoscale cannot be ruled out and additional studies by TEM observation will be carried out to help clarify this issue.

### 3.2.3 Figure of merit (ZT)

The figure of merit, ZT, is shown in Fig. 9. ZT shows a trend of increasing in magnitude with increasing temperature, typical for Al-doped ZnO ceramics.\(^{(16)}\) A maximum value of $ZT = 0.07$ is obtained at 750°C for the 1 at% Al-doped sample. This value is comparable with that from previous reports for Al-doped ZnO thermoelectrics sintered in air at 1400°C.\(^{(13)}\) However, there is a reduction of ZT with increasing Mn doping concentration. This is due to the increasing resistivity accompanying increasing Mn dopant content. Thus, despite the reduction in thermal conductivity due to the Mn dopant addition and the small difference in electronegativity between Mn and Zn dopants, the increase of resistivity due to carrier scattering caused by precipitate formation and alloy scattering was too large and resulted in an overall decrease of ZT.

Previous reports have attempted to establish a correlation between material properties and the potential for increase of ZT through thermal conductivity reduction by solid solution alloying.\(^{(41)}\) It is found that material systems with a low Grüneisen parameter ($\gamma$) and high bond stiffness stand to gain the most improvement in ZT through alloying. In contrast, in material systems such as PbTe-PbSe, which have a fairly high Grüneisen parameter, improvement in ZT through alloying was not realized.\(^{(3)}\) ZnO has a fairly low Grüneisen parameter, $\gamma = 0.75$\(^{(45)}\) similar to Si-Ge ($\gamma = 0.6$)\(^{(45)}\) and considerably lower than PbTe-PbSe ($\gamma = 1.4$).\(^{(41)}\) The bulk modulus, $B$, an indicator of bond stiffness, is also higher for the ZnO system ($B = 142.6$ GPa)\(^{(13)}\) than for Silicon ($B = 98$ GPa)\(^{(13)}\) or Ge ($B = 77.2$ GPa).\(^{(13)}\) Both the low Grüneisen parameter and high bulk modulus of ZnO in combination with its high intrinsic lattice thermal conductivity (another parameter cited as having a strong correlation with potential for $\kappa$ reduction)\(^{(16)}\) of 60 W/($m$K$^2$) would indicate that there is potential for ZT improvement in ZnO by alloying.

Despite the apparent potential for ZT improvement through alloying in ZnO, the results of previous studies\(^{(3)}\) as well as the current study show no improvement in ZT through alloying with either Mg\(^{(13)}\) or Mn. It has been shown that there is a trade-off between thermal conductivity reduction and alloy scattering for solid solution alloying of thermoelectric materials.\(^{(41)}\) If a large mass contrast between the host lattice atom and the dopant ion can be achieved, the increase of ZT through thermal conductivity reduction will be increased, as indicated by Eq. (7), where the scattering parameter is shown to increase by the square of the mass contrast. Likewise, choosing a dopant with a high solubility is also important, since the scattering parameter will increase linearly with dopant concentration.

There are few dopants with a solubility even exceeding 5 at% in ZnO. Among these are Mn,\(^{(13)}\) Mg\(^{(45)}\) and Co.\(^{(5)}\) The mass contrast of Mn with Zn is approx. 16%. This mass contrast is not as high as for some systems such as Si-Ge (61%) but is still significant enough to achieve thermal conductivity reduction, as evidenced by the thermal conductivity values achieved in the present study (40% reduction at RT for 2 at% Mn doping). The additional advantage of the Mn dopant is the close electronegativity to Zn. Since the alloy scattering parameter, $u$, is considered to have a correlation with the electron affinity difference between alloying element and the element of the host lattice to be substituted for,\(^{(41)}\) this small electronegativity difference could potentially reduce the effect of alloy scattering and result in improved ZT. However, increases in ZT were not realized in the present study, suggesting that the alloy scattering could not be sufficiently diminished by use of the Mn dopant to realize ZT improvement through thermal conductivity reduction.

Use of a dopant with a larger mass contrast with ZnO could be considered for achieving ZT improvement but even the use of Mg could not improve the ZT of ZnO, suggesting that either the mass contrast (63%) was not significant enough or that the alloy scattering was too large.\(^{(13)}\) The potential to increase the ZT of ZnO through alloying to reduce thermal conductivity still exists; however, due to the limited number of dopants with high solubility in ZnO, prospects may be limited. One possibility is doping with one or several elements having a solubility of at least several at%, and also having a large mass contrast and a minimal electronegativity contrast with the host ions of ZnO.

Other methods to reduce the thermal conductivity or improve the Seebeck coefficient without significantly affecting the electrical conductivity may be more effective for realizing increases in the ZT of ZnO. Previous studies have suggested that nanoscale phase separation or spinodal decomposition may occur in Mn-doped\(^{(16)}\) or Mn-Al co-doped ZnO.\(^{(17)}\) Although, a ZT improvement due to these mechanisms was not observed in this study,
other dopants could be identified which may undergo spinodal decomposition or nucleation and growth with the ZnO system. If nanostructures having coherent interfaces can be formed through these mechanisms, an increased $ZT$ could potentially be realized by thermal conductivity reduction with little or no impact on electrical resistivity.

4. Summary

The microstructure and thermoelectric properties of Mn–Al co-doped ZnO ceramics have been analyzed and clear trends related to Mn doping were observed. Al-doping leads to a microstructure of fine spinel precipitates (ZnAl$_2$O$_4$). As Mn content increases, these precipitates increase in size and volume fraction and the power factor and $ZT$ of ZnO were reduced with increasing Mn doping due to Mn substitutional ions acting as point defects to scatter short wavelength phonons. Overall, the increasing Mn doping was observed. This is attributed to an increase in resistivity. The Seebeck coefficient increased in absolute value only at significant (10 at%) Mn dopant levels, caused by a high volume of spinel precipitates or increased low energy carrier scattering at high potential barrier grain boundaries. Thermal conductivity showed a decrease with increased low energy carrier scattering at high potential barrier grain boundaries. Thermal conductivity showed a decrease with increased Mn doping due to Mn substitutional ions acting as point defects to scatter short wavelength phonons. Overall, the power factor and $ZT$ of ZnO were reduced with increasing Mn doping due to the increase in resistivity.

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