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1 The Influence of α - and γ -Al₂O₃ Phases on the 2 Thermoelectric Properties of Al-doped ZnO

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10 Abstract:

11 A systematic investigation on the microstructure and thermoelectric properties of Al-doped ZnO
12 using α - and γ -Al₂O₃ as dopants was conducted in order to understand the doping effect and its
13 mechanism. The samples were prepared by the spark plasma sintering technique from precursors
14 calcined at various temperatures. Clear differences in microstructure and thermoelectric properties
15 were observed between the samples doped with α - and γ -Al₂O₃. At any given calcination
16 temperature, γ -Al₂O₃ resulted in the formation of a larger amount of the ZnAl₂O₄ phase in the Al-
17 doped ZnO samples. The average grain size was found to be smaller for the γ -Al₂O₃-doped
18 samples than that for the α -Al₂O₃-doped ones under the same sintering condition. It is proposed
19 that the ZnAl₂O₄ phase is the reason for the observed suppression of grain growth and also for the
20 slightly reduced lattice thermal conductivity exhibited by these samples. The γ -Al₂O₃ promoted the
21 substitution for donor impurities in ZnO, thus resulting in shrinkage of the unit cell volume and an
22 increase in the electrical conductivity compared with the α -Al₂O₃-doped ZnO. At a calcination
23 temperature of 1173K, the γ -Al₂O₃-doped sample showed a ZT value of 0.17 at 1173K, which is
24 27% higher than that of the α -Al₂O₃-doped sample.

25 *Key words: thermoelectric oxide, Al-doped ZnO, α - and γ -Al₂O₃, ZnAl₂O₄*
26 *formation kinetics.*

28 1. Introduction

29 Thermoelectric oxide materials are strong candidates for high temperature
30 power generation from waste heat. The promising high temperature n-type

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thermoelectric properties of Al-doped ZnO were first brought to the public sight by Ohtaki et al. in 1996 [1]. Recently, a figure-of-merit, ZT of 0.44 at 1000 K was obtained for nanostructured Al-doped ZnO [2], and again this showed the possibility of using ZnO for low-cost practical waste heat harvesting. In the last few years, intensive investigations have been targeted to improve the thermoelectric properties and the preparation conditions of Al-doped ZnO [3,4,5,18], but little attention has been paid to the choice of which phases of Al_2O_3 should be used as the dopant. This is probably one of the reasons for the controversial results reported by many research groups on the thermoelectric performance of Al-doped ZnO. Therefore, it is noteworthy to investigate systematically the influences of using different phases of Al_2O_3 as dopants on the thermoelectric properties of Al-doped ZnO. In fact, the α - and γ -phases of Al_2O_3 have different crystal structures and physical properties with their specific reaction kinetics with ZnO [6,7,8]. Moreover, the phase transition of Al_2O_3 is temperature dependent, suggesting that the synthesis temperature of Al-doped ZnO is crucial and can result in different material properties.

From this point of view, we have conducted a systematic investigation of the microstructure and the thermoelectric properties of Al-doped ZnO synthesized by various heat treatments using two different phases of Al_2O_3 as dopants: γ - Al_2O_3 with a defect spinel structure and α - Al_2O_3 with the corundum structure. We observed a noticeable difference in the microstructure and thermoelectric properties between α - and γ - Al_2O_3 -doped ZnO when the synthesis temperature was lower than 1273 K. The correlations between the thermoelectric properties, microstructure evolutions, and the solid state reaction kinetics of the secondary phases are discussed herein.

2. Experimental Procedure

The starting materials used in these investigations are: ZnO (99+% 40-100 nm APS powder, Alfa-Aesar), γ - Al_2O_3 (99.5% 45-55 nm APS Powder, Alfa-Aesar), and α - Al_2O_3 (99.5% 0.9-2.2 Micron APS Powder, Alfa-Aesar).

The synthesis of Al-doped ZnO ceramics: Aluminum oxide (γ - Al_2O_3 or α - Al_2O_3) was mixed with ZnO at a molar ratio of 1:98 (the atomic ratio of Al:Zn = 2:98) by ethanol-aided roll milling using ceramic balls for 24 h. The resulting mixtures were then dried at room temperature for 24 h followed by further drying

at 403 K for 3 h. The dried powders were put into porcelain boats and calcined at various temperatures (973, 1073, 1173, and 1273 K) under N_2 for 1 h. After calcination, the powders were sieved using a 300 mesh sieve, corresponding to a mean particle size of 48 μm . The precursors were densified using optimized conditions into compact bulk pellets by spark plasma sintering (SPS) at 1173 K for 5 min in argon under a uniaxial pressure of 50 MPa. The six sintered samples are denoted as γ -973, α -1073, γ -1073, α -1173, γ -1173, α -1273 according to the phase of Al_2O_3 used and the calcination temperatures. These samples and their precursors were examined by power X-ray diffraction (XRD) on a Bruker D8 diffractometer (Bruker, Germany) using $Cu-K\alpha$ radiation. The density of the samples was measured on an AccuPyc-1340 Pycnometer. A scanning electron microscope (SEM) (Supra, Carl Zeiss, Inc. Germany) equipped with an EDX spectrometer was used to observe the microstructures of the samples. The measurements of the electrical resistivity and the Seebeck coefficient were carried out on an ULVAC-RIKO ZEM-3 from room temperature up to 1173 K under a low pressure of helium atmosphere. The thermal conductivity was determined from the thermal diffusivity obtained by the laser flash method (a Netzch FLA-457) and the specific heat capacity calculated by the Dulong-Petit relation.

3. Results and discussion

The relative density of the bulk sintered ZnO samples doped with $\alpha/\gamma-Al_2O_3$ was found to be all above 95% regardless of the calcination temperature. X-ray diffraction analysis for these samples showed that most of the observed XRD peaks (see Fig. 1a) are assigned to those of pure ZnO phase (ICDD card PDF#36-1451). It also reveals in the inset of Fig. 1 that the peak at $2\theta = 36.83^\circ$ assigned to the strongest peak of $ZnAl_2O_4$ gahnite phase [14]. Comparing this peak over the samples, it seems as if those peaks of the α -1073 and γ -973 samples are more diffused than those of the samples with higher calcination temperature. The cell volume monotonically decreased with increasing calcination temperature for both α - and γ - Al_2O_3 -doped samples (see Fig. 1b). The ionic radius of Al^{3+} (0.039 nm, 4-fold coordination) is smaller than that of Zn^{2+} (0.060 nm, 4-fold coordination) [17], suggesting that the decrease of the unit cell volume may originate from the substitutions of Al^{3+} at Zn-sites promoted by the elevated calcination temperature.

96 It should also be noted that the unit cell volume was smaller for the γ -1073 and γ -
97 1173 samples than that for the α -1073 and α -1173 samples, respectively.

98 Fig. 2a-f shows the SEM micrographs of fracture surfaces and the EDX
99 analysis from a selected area of α/γ -Al₂O₃-doped ZnO samples sintered by SPS.
100 Fig. 2a-e reveal that besides the ZnO grains with the size of several micrometers,
101 there exist some interspersed nano-sized grains, which precipitate within the ZnO
102 grain interiors or at the grain boundaries. An EDX line scan was taken across the
103 nanoprecipitates (see Figure 2e, f), showing that these nano-grains have enriched
104 Al concentrations. This observation, together with the ZnAl₂O₄ gahnite phase
105 detected by XRD, suggests the formation of ZnAl₂O₄ precipitates in these
106 samples. A difference in the grain growth was also clearly observed as the
107 calcination temperature increased. At the same calcination temperature the γ -
108 Al₂O₃-doped samples have smaller average grain sizes ($\sim 1\mu\text{m}$) than those of the
109 α -Al₂O₃-doped samples ($\sim 1.5\mu\text{m}$), as shown in Figs. 2b and 2c. This difference in
110 grain size would be caused by the boundary pinning effect of the ZnAl₂O₄
111 nanoprecipitates during grain growth [9]. These results indicate that the formation
112 rate of ZnAl₂O₄ is closely correlated to the phases of the Al₂O₃ precursors, and
113 this will be discussed in the following section with relation to the kinetic
114 calculation.

115 Fig. 3 shows the temperature dependence of the electrical conductivity (σ) of
116 α/γ -Al₂O₃-doped ZnO samples. All the investigated samples showed a
117 semiconducting behavior over the whole measured temperature range, i.e. the
118 electrical conductivity increases with increasing temperature. The calculated
119 activation energy for electronic conduction of the α -1073 sample changed from
120 ~ 17 meV to ~ 304 meV at and above 770 K. With increasing calcination
121 temperature, this change became less pronounced suggesting that more carriers
122 are available for conduction. For both the α - and the γ -Al₂O₃-doped ZnO samples,
123 the electrical conductivity increased with increasing calcination temperature. The
124 σ values of the γ -1073 and γ -1173 samples are notably higher than those of the α -
125 1073 and α -1173 samples, respectively. Shown in the inset of Fig. 3 is the
126 electrical conductivity, which was extracted from the data at 1173 K, as a function
127 of the calcination temperature. It appears that the change of σ is consistent with
128 the change of the unit cell volume (Fig. 1b), which could be attributed to the Al
129 substitution at the Zn-site according to the following equation [10]:

130

131 From Eq. 1, one can see that the substitution of Zn^{2+} by Al^{3+} is the reason for
132 the unit cell volume shrinkage which may result in the increase in the donor
133 impurity concentration [11], thus providing excess charged carriers available for
134 electrical conduction.

135 Fig. 4 shows the temperature dependence of the Seebeck coefficients, S , of the
136 α/γ - Al_2O_3 -doped samples. The S values of all the samples are negative over the
137 whole temperature range examined, indicating n-type conduction. As shown in the
138 inset of Fig. 4, at 1173 K, the α/γ - Al_2O_3 -doped samples exhibit a monotonic
139 decrease of S with increasing calcination temperature. According to Jonker and
140 the Pisarenko relation, a simple broad band model for extrinsic n-type
141 semiconductors with negligible hole conduction can describe this behavior [12],

$$\sigma = ne\mu \quad (2)$$

$$|S| = A'Tm_d^* \left(\frac{\pi}{3n}\right)^{2/3} \quad (3)$$

142

143 where n is the carrier concentration, e is the electric charge of the carrier, μ is the
144 mobility, A' is a constant, T is the absolute temperature, m_d^* is a density of the
145 state (DOS) effective mass at the Fermi level. As the electrical conductivity (σ)
146 and the Seebeck coefficient (S) are both a function of the carrier concentration (n),
147 Eq. 2 and 3 clearly show that a higher n value causes an increase in σ but a
148 decrease in $|S|$, which well explains the tendency observed in Fig.4. For example,
149 the α -1273 sample with the highest electrical conductivity showed the smallest $|S|$
150 in the investigated temperature region.

151 The total thermal conductivity (κ) of the sintered samples using different α/γ -
152 Al_2O_3 and various calcination temperatures is shown in Fig. 5. In general, κ
153 rapidly decreases with increasing temperature, which is in good agreement with
154 the result reported by Ohtaki et al [13]. It can also be seen from Fig. 5 that κ tends
155 to increase with increasing calcination temperature. We estimated the electronic
156 contribution κ_e using the Wiedemann–Franz law and found that the increase in κ
157 with increasing calcination temperature is attributed to the increase in κ_e ,
158 particularly in the high temperature region. Although the total κ values at 1173 K

as a function of the calcination temperature (see Fig. 5 inset) appeared to be virtually the same for both α - and γ -Al₂O₃-doped samples, the lattice thermal conductivity, κ_L , of the samples at 1173 K was somewhat smaller for the γ -1073 and γ -1173 samples (5.06 Wm⁻¹K⁻¹ and 5.15 Wm⁻¹K⁻¹, respectively) than those of the α -1073 α -1173 samples (5.31 Wm⁻¹K⁻¹ and 5.43 Wm⁻¹K⁻¹, respectively). As illustrated by the microstructure in Fig. 2, the reason for the lower conductivity in the γ -1073 sample as compared with the α -1073 sample is probably due to the formation of disperse ZnAl₂O₄ nanoprecipitates in γ -1073 sample which might act as a phonon scattering center.

The power factor, $S^2\sigma$, of the samples is presented in Fig. 6. It shows that the power factor values of γ -1073 and γ -1173 are notably higher than that of α -1073 and α -1173. Also, the power factor monotonically increases with increasing calcination temperature, as shown in the inset of Fig. 6. The higher power factor observed for the γ -Al₂O₃-doped samples was mainly due to the increase in their electrical conductivity as compared to that of the α -Al₂O₃-doped samples. At 1173K, the highest power factor of $\sim 8.31 \times 10^{-4} \text{ Wm}^{-1} \text{ K}^{-2}$ measured in this study is comparable to the value of $\sim 8 - 15 \times 10^{-4} \text{ Wm}^{-1} \text{ K}^{-2}$ reported by Ohtaki et al [1] and the value of $\sim 8.3 \times 10^{-4} \text{ Wm}^{-1} \text{ K}^{-2}$ reported by Jood et al [2] for Al-doped ZnO.

The dimensionless figure of merit, ZT , is given in Fig. 7, showing that the ZT values of γ -1073 and γ -1173 are also higher than those of α -1073 and α -1173. At 1173K, the γ -1173 sample with the highest power factor attained a ZT of 0.17, which is about 27% higher than that for the α -Al₂O₃-doped counterpart at the same temperature. The highest ZT value of our sample is on the same order of the one reported by Ohtaki et al [1] at the same temperature. It should be noted here that the higher ZT value ($ZT \sim 0.44$ at 1000 K) reported by Jood et al is mainly due to the suppression in the thermal conductivity of the sample by nanostructuring [2]. Nevertheless, our ZT value is higher than the ones reported by Cai et al [10] and Tanaka et al [16] at the same temperature.

We found that the ZnO samples doped with γ -Al₂O₃ showed a better thermoelectric performance compared to those doped with α -Al₂O₃, when calcined at a temperature lower than 1273 K. At a calcination temperature higher than 1273 K, the difference in the thermoelectric properties gradually diminishes due to the intrinsic phase transformation of γ -Al₂O₃ to α -Al₂O₃.

192 To understand these observations, we looked into the kinetics and mechanism
193 of the reaction between ZnO and Al₂O₃. The formation of the secondary phase,
194 ZnAl₂O₄, resulting from the reaction between ZnO and Al₂O₃ is well known, and
195 can be represented as follows:

196 It should be noted that the formation of ZnAl₂O₄ cannot be avoided during the
197 preparation process of Al-doped ZnO [2,4,5]. The limited solubility of Al atom
198 into ZnO [14] could be one of the reasons. According to the thermodynamics
199 description of the reaction (Eq. 4) suggested by K. T. Jacob [6], the standard
200 Gibbs free energy change (ΔG) of the ZnAl₂O₄ formation from the reaction of α -
201 Al₂O₃ and ZnO equals $-45.0081 + 0.0066T$ kJ, indicating that the formation of
202 ZnAl₂O₄ is favored from room temperature to far above 1673 K ($\Delta G \leq 0$). The
203 reaction rate is kinetically controlled by solid state diffusion [7,8].

205 Fig. 8 shows the calculated reaction time course of ZnAl₂O₄ formation using
206 Jander's model for powder reactions. According to this model, it is assumed that
207 Al₂O₃ particles are embedded in a quasi-continuous ZnO medium. The reaction
208 rate of the ZnAl₂O₄ formation from ZnO and Al₂O₃ is diffusion-controlled and
209 hence follows a parabolic rate law:

$$\left[1 - (1 - W)^{\frac{1}{3}}\right]^2 = 2 \cdot k_p \cdot t / r_o^2 \quad (5)$$

210 where W is the weight fraction of the reacted Al₂O₃, k_p is the practical parabolic
211 rate constant, t is the reaction time and r_o is the particle size of Al₂O₃ powder. The
212 practical parabolic rate constant k_p follows the Arrhenius law:
213

$$k_p = A \cdot e^{-\frac{E_a}{RT}} \quad (6)$$

214 where A is pre-exponential factor (a term which includes factors like the
215 frequency of collisions and their orientation), E_a is the activation energy, R is the
216 gas constant, T is temperature. By combining Eq. 5 and Eq. 6, one can obtain:
217

$$W = 1 - \left[1 - (2A \cdot t)^{\frac{1}{2}} \cdot e^{-\frac{E_a}{2RT}} \cdot r_o^{-1}\right]^3 \quad (7)$$

218 According to the experimental data reported by Tsuchida et al [8], the parameters
219 of A and E_a can be obtained by Arrhenius fitting. A equals $18076 \mu\text{m}^2 \text{min}^{-1}$. E_a for
220 α -Al₂O₃ and γ -Al₂O₃ equals 4.9 and 2.04 eV, respectively. r_o equals the average
221 particle size of Al₂O₃ powder. Using Eq. 7, the reacted Al₂O₃ fraction can be
222

223 plotted as a function of time. As shown in Fig. 8a, the reaction rate of γ - Al_2O_3
 224 with ZnO is significantly higher than that of α - Al_2O_3 at the same temperature due
 225 to the lower activation energy of γ - Al_2O_3 . From these data, we calculated the
 226 percentage of reaction completed after 1 hour as a function of the calcination
 227 temperature, and the results are shown in Fig. 8b. A clear correlation was found
 228 between the percentage of the reacted Al_2O_3 and the thermoelectric properties of
 229 these samples. The α -1073 sample with the smallest calculated percentage of the
 230 reacted Al_2O_3 showed the lowest σ values, while the α -1273 and γ -1173 samples
 231 with almost fully reacted Al_2O_3 showed relatively high σ . Accordingly, the
 232 electrical conductivities of the γ -1073/1173 samples were higher than those of the
 233 α -1073/1173 samples (Fig. 3). Also, the smaller grains size of the γ - Al_2O_3 -doped
 234 samples compared to that of the α - Al_2O_3 -doped ones may be explained by a
 235 stronger boundary pinning effect during grain growth caused by a larger number
 236 of ZnAl_2O_4 nanoprecipitates. This is presumably due to the faster reaction and
 237 larger fraction of ZnAl_2O_4 formation for the γ - Al_2O_3 -doped samples.

238 The detailed mechanisms of the reaction between ZnO and Al_2O_3 have already
 239 been studied by Branson [7] and Tsuchida et al [8]. Branson carried out marker
 240 transport experiments at the interfaces between ZnO, ZnAl_2O_4 and Al_2O_3 , and
 241 pointed out that the formation of ZnAl_2O_4 is a result of Zn ions diffusing into
 242 Al_2O_3 . Later, Tsuchida et al. not only showed evidence to support this result but
 243 also revealed the reason for the ZnAl_2O_4 formation speed. They pointed out that
 244 the reaction of α or γ - Al_2O_3 with ZnO resulted in different degrees of crystallinity
 245 of the product layers, i.e. formation of ZnAl_2O_4 as “hereditary structure” [8].
 246 Owing to the different degrees of crystallinity, the diffusivity of Zn ions in
 247 ZnAl_2O_4 can be varied. As a result, in the γ - Al_2O_3 , the formation of a defect
 248 ZnAl_2O_4 layer with a higher diffusivity of the Zn ions is observed.
 249 Correspondingly, α - Al_2O_3 results in a nearly perfect, defect free ZnAl_2O_4 structure
 250 with a lower diffusivity of the Zn ions and higher activation energy.

251 However, the faster formation of the ZnAl_2O_4 phase is not likely to be the
 252 direct reason for the increase of the electrical conductivity in the γ - Al_2O_3 -doped
 253 samples, since the ZnAl_2O_4 phase is reported to be unfavorable for the electrical
 254 conductivity [1]. By comparing Fig. 1b and 8b, the unit cell volume shrinkage
 255 increases along with increasing the ZnAl_2O_4 phase formation, indicating that the

substitution of Al for Zn simultaneously occurred during the formation of the ZnAl₂O₄ phase, which can be represented as:

According to the previous investigations by Branson, the diffusion of Al toward ZnO does not contribute to the formation of ZnAl₂O₄ [7]. His explanation of the reaction between ZnO and Al₂O₃ did not take the Al diffusion into consideration. From our experimental results and investigations by other groups who observed the existence of Al diffusion into ZnO using HRTEM [15], a modified Branson's schematic diagram of the reaction process is proposed and the details is presented in Fig. 9. It includes a counter-diffusion between ZnO and Al₂O₃. The formation of ZnAl₂O₄ is only caused by the diffusion of Zn to Al₂O₃, while the Al substitution for Zn results from the diffusion of Al into ZnO. The disordered structure of γ -Al₂O₃ may lead to the disordered product layers of ZnAl₂O₄. The Al and Zn ions would be easier to diffuse through the disordered product layer. It promotes both the formation of ZnAl₂O₄ and the substitutions of Al for Zn as donor impurities in ZnO, thus resulting in enhanced grain boundary pinning by ZnAl₂O₄ and the observed higher electrical conductivity of the γ -Al₂O₃-doped ZnO than that of the α -Al₂O₃-doped counterpart.

4. Conclusions

In summary, we observed a close correlation between the thermoelectric properties, microstructure evolution, and the solid state reaction kinetics of the ZnAl₂O₄ formation using Jander's solid-state reaction model. At a given calcinations temperature, the addition of γ -Al₂O₃ resulted in a larger fraction of the ZnAl₂O₄ formation in the Al-doped ZnO samples, which also inhibited the grain growth and slightly reduced the lattice thermal conductivity. The higher diffusion rate of Al observed for the γ -Al₂O₃ resulted in a larger unit cell volume shrinkage and higher electrical conductivity as compared with the α -Al₂O₃-doped ZnO. As a consequence, γ -Al₂O₃-doped ZnO exhibited a higher ZT than the α -Al₂O₃-doped counterpart under the same preparation conditions with calcination temperatures lower than 1273 K.

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Figure captions

- Fig. 1. (a) XRD patterns of α/γ -Al₂O₃-doped ZnO with different calcination temperatures (from 973 to 1273 K). The dotted box magnified as the inset shows the position of the strongest peak from ZnAl₂O₄. (b) The unit cell volume obtained from the lattice parameter refinement as a function of the calcination temperature.
- Fig. 2. SEM photographs of the fracture surfaces of α/γ -Al₂O₃-doped ZnO. (a) γ -973, (b) γ -1073, (c) α -1073, (d) α -1273, (e) a representative high-magnification SEM image of the ZnAl₂O₄ nanoprecipitates. EDX line scans of Zn, O, and Al K α_1 X-ray peaks obtained along the yellow arrow are shown in (f).
- Fig. 3. Temperature dependence of the electrical conductivity of α/γ -Al₂O₃-doped ZnO samples. The inset shows the electrical conductivity at 1173 K as a function of the calcination temperature.
- Fig. 4. Temperature dependence of the Seebeck coefficient of α/γ -Al₂O₃-doped ZnO samples. The inset shows the Seebeck coefficient at 1173 K as a function of the calcination temperature.
- Fig. 5. Temperature dependence of the thermal conductivity of α/γ -Al₂O₃-doped ZnO samples. The inset shows the thermal conductivity at 1173 K as a function of the calcination temperature.
- Fig. 6. Temperature dependence of the power factor of α/γ -Al₂O₃-doped ZnO samples. The inset shows the power factor at 1173 K as a function of the calcination temperature.
- Fig. 7. Temperature dependence of ZT of α/γ -Al₂O₃-doped ZnO samples. The inset shows the ZT values at 1173 K as a function of the calcination temperature.
- Fig.8. (a) The calculated reaction time course as a weight fraction of reacted Al₂O₃ for the ZnAl₂O₄ formation. (b) The percentage of reaction completed after 1 hour as a function of the calcination temperature.
- Fig. 9. A modified schematic diagram for the solid-state reaction process of ZnO and Al₂O₃ based on Branson's investigation.

359

360 Fig. 1

361

362 Fig. 1. (a) XRD patterns of α/γ - Al_2O_3 -doped ZnO with different calcination temperatures (from
363 973 to 1273 K). The dotted box magnified as the inset shows the position of the strongest peak
364 from ZnAl_2O_4 . (b) The unit cell volume obtained from the lattice parameter refinement as a
365 function of the calcination temperature.

366

367 Fig. 2

368

369 Fig. 2. SEM photographs of the fracture surfaces of α/γ - Al_2O_3 -doped ZnO. (a) γ -973, (b) γ -1073,370 (c) α -1073, (d) α -1273, (e) a representative high-magnification SEM image of the ZnAl_2O_4 371 nanoprecipitates. EDX line scans of Zn, O, and Al $\text{K}\alpha_1$ X-ray peaks obtained along the yellow

372 arrow are shown in (f).

373

374 Fig. 3

375

376 Fig. 3. Temperature dependence of the electrical conductivity of α/γ - Al_2O_3 -doped ZnO samples.

377 The inset shows the electrical conductivity at 1173 K as a function of the calcination temperature.

378

379 Fig. 4

380

381 Fig. 4. Temperature dependence of the Seebeck coefficient of α/γ - Al_2O_3 -doped ZnO samples. The
 382 inset shows the Seebeck coefficient at 1173 K as a function of the calcination temperature.

383

384 Fig. 5

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386

387 Fig. 5. Temperature dependence of the thermal conductivity of $\alpha/\gamma\text{-Al}_2\text{O}_3$ -doped ZnO samples.

388 The inset shows the thermal conductivity at 1173 K as a function of the calcination temperature.

389

390 Fig. 6

391

392 Fig. 6. Temperature dependence of the power factor of α/γ - Al_2O_3 -doped ZnO samples. The inset
 393 shows the power factor at 1173 K as a function of the calcination temperature.

394

395 Fig. 7

396

397 Fig. 7. Temperature dependence of ZT of α/γ - Al_2O_3 -doped ZnO samples. The inset shows the ZT
 398 values at 1173 K as a function of the calcination temperature.

399

400 Fig. 8

Fig.8. (a) The calculated reaction time course as a weight fraction of reacted Al_2O_3 for the ZnAl_2O_4 formation. (b) The percentage of reaction completed after 1 hour as a function of the calcination temperature.

407 Fig. 9

408

409 Fig. 9. A modified schematic diagram for the solid-state reaction process of ZnO and Al₂O₃ based
 410 on Branson's investigation.

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Highlights

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- Clear differences in microstructure and thermoelectric properties were observed between the γ -Al₂O₃-doped ZnO and α -Al₂O₃-doped ZnO.
- γ -Al₂O₃-doped ZnO obtained a higher ZT than that of α -Al₂O₃-doped ZnO with the same preparation condition lower than 1273K.
- The differences in microstructure and thermoelectric properties with α -/ γ -Al₂O₃-doped ZnO can be correlated to the solid state reaction kinetics of ZnAl₂O₄ formation.
- A possible mechanism of ZnAl₂O₄ formation was proposed.