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Li Han, Ngo Van Nong, Le Thanh Hung, Tim Holgate, Nini Pryds, Michitaka Ohtaki, Søren Linderorth

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

3 Li Han,^{a*} Ngo Van Nong,^a Le Thanh Hung,^a Tim Holgate,^a Nini Pryds,^a
4 Michitaka Ohtaki^b and Søren Linderøth^a

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

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

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

* Corresponding author at: DTU Energy Conversion, DTU Risø Campus, Frederiksborgvej 399,
4000 Roskilde, Denmark

E-mail address: ihan@dtu.dk

31 thermoelectric properties of Al-doped ZnO were first brought to the public sight
32 by Ohtaki et al. in 1996 [1]. Recently, a figure-of-merit, ZT of 0.44 at 1000 K was
33 obtained for nanostructured Al-doped ZnO [2], and again this showed the
34 possibility of using ZnO for low-cost practical waste heat harvesting. In the last
35 few years, intensive investigations have been targeted to improve the
36 thermoelectric properties and the preparation conditions of Al-doped ZnO
37 [3,4,5,18], but little attention has been paid to the choice of which phases of Al₂O₃
38 should be used as the dopant. This is probably one of the reasons for the
39 controversial results reported by many research groups on the thermoelectric
40 performance of Al-doped ZnO. Therefore, it is noteworthy to investigate
41 systematically the influences of using different phases of Al₂O₃ as dopants on the
42 thermoelectric properties of Al-doped ZnO. In fact, the α - and γ -phases of Al₂O₃
43 have different crystal structures and physical properties with their specific
44 reaction kinetics with ZnO [6,7,8]. Moreover, the phase transition of Al₂O₃ is
45 temperature dependent, suggesting that the synthesis temperature of Al-doped
46 ZnO is crucial and can result in different material properties.

47 From this point of view, we have conducted a systematic investigation of the
48 microstructure and the thermoelectric properties of Al-doped ZnO synthesized by
49 various heat treatments using two different phases of Al₂O₃ as dopants: γ -Al₂O₃
50 with a defect spinel structure and α -Al₂O₃ with the corundum structure. We
51 observed a noticeable difference in the microstructure and thermoelectric
52 properties between α - and γ -Al₂O₃-doped ZnO when the synthesis temperature
53 was lower than 1273 K. The correlations between the thermoelectric properties,
54 microstructure evolutions, and the solid state reaction kinetics of the secondary
55 phases are discussed herein.

56 2. Experimental Procedure

57 The starting materials used in these investigations are: ZnO (99+% 40-100 nm
58 APS powder, Alfa-Aesar), γ -Al₂O₃ (99.5% 45-55 nm APS Powder, Alfa-Aesar),
59 and α -Al₂O₃ (99.5% 0.9-2.2 Micron APS Powder, Alfa-Aesar).

60 The synthesis of Al-doped ZnO ceramics: Aluminum oxide (γ -Al₂O₃ or α -
61 Al₂O₃) was mixed with ZnO at a molar ratio of 1:98 (the atomic ratio of Al:Zn =
62 2:98) by ethanol-aided roll milling using ceramic balls for 24 h. The resulting
63 mixtures were then dried at room temperature for 24 h followed by further drying

64 at 403 K for 3 h. The dried powders were put into porcelain boats and calcined at
65 various temperatures (973, 1073, 1173, and 1273 K) under N₂ for 1 h. After
66 calcination, the powders were sieved using a 300 mesh sieve, corresponding to a
67 mean particle size of 48 μm. The precursors were densified using optimized
68 conditions into compact bulk pellets by spark plasma sintering (SPS) at 1173 K
69 for 5 min in argon under a uniaxial pressure of 50 MPa. The six sintered samples
70 are denoted as γ-973, α-1073, γ-1073, α-1173, γ-1173, α-1273 according to the
71 phase of Al₂O₃ used and the calcination temperatures. These samples and their
72 precursors were examined by power X-ray diffraction (XRD) on a Bruker D8
73 diffractometer (Bruker, Germany) using Cu-Kα radiation. The density of the
74 samples was measured on an AccuPyc-1340 Pycnometer. A scanning electron
75 microscope (SEM) (Supra, Carl Zeiss, Inc. Germany) equipped with an EDX
76 spectrometer was used to observe the microstructures of the samples. The
77 measurements of the electrical resistivity and the Seebeck coefficient were carried
78 out on an ULVAC-RIKO ZEM-3 from room temperature up to 1173 K under a
79 low pressure of helium atmosphere. The thermal conductivity was determined
80 from the thermal diffusivity obtained by the laser flash method (a Netzch FLA-
81 457) and the specific heat capacity calculated by the Dulong-Petit relation.

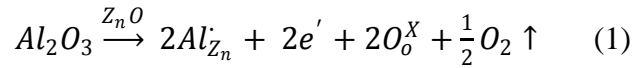
82 3. Results and discussion

83 The relative density of the bulk sintered ZnO samples doped with α/γ-Al₂O₃
84 was found to be all above 95% regardless of the calcination temperature. X-ray
85 diffraction analysis for these samples showed that most of the observed XRD
86 peaks (see Fig. 1a) are assigned to those of pure ZnO phase (ICDD card PDF#36-
87 1451). It also reveals in the inset of Fig. 1 that the peak at $2\theta = 36.83^\circ$ assigned to
88 the strongest peak of ZnAl₂O₄ gahnite phase [14]. Comparing this peak over the
89 samples, it seems as if those peaks of the α-1073 and γ-973 samples are more
90 diffused than those of the samples with higher calcination temperature. The cell
91 volume monotonically decreased with increasing calcination temperature for both
92 α- and γ-Al₂O₃-doped samples (see Fig. 1b). The ionic radius of Al³⁺ (0.039 nm,
93 4-fold coordination) is smaller than that of Zn²⁺ (0.060 nm, 4-fold coordination)
94 [17], suggesting that the decrease of the unit cell volume may originate from the
95 substitutions of Al³⁺ 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 - Al_2O_3 -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 ZnAl_2O_4 gahnite phase
105 detected by XRD, suggests the formation of ZnAl_2O_4 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 Al_2O_3 -doped samples have smaller average grain sizes ($\sim 1\mu\text{m}$) than those of the
109 α - Al_2O_3 -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 ZnAl_2O_4
111 nanoprecipitates during grain growth [9]. These results indicate that the formation
112 rate of ZnAl_2O_4 is closely correlated to the phases of the Al_2O_3 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 - Al_2O_3 -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 - Al_2O_3 -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

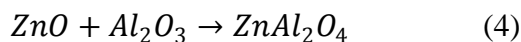
159 as a function of the calcination temperature (see Fig. 5 inset) appeared to be
160 virtually the same for both α - and γ -Al₂O₃-doped samples, the lattice thermal
161 conductivity, κ_L , of the samples at 1173 K was somewhat smaller for the γ -1073
162 and γ -1173 samples (5.06 Wm⁻¹K⁻¹ and 5.15 Wm⁻¹K⁻¹,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

168 The power factor, $S^2\sigma$, of the samples is presented in Fig. 6. It shows that the
169 power factor values of γ -1073 and γ -1173 are notably higher than that of α -1073
170 and α -1173. Also, the power factor monotonically increases with increasing
171 calcination temperature, as shown in the inset of Fig. 6. The higher power factor
172 observed for the γ -Al₂O₃-doped samples was mainly due to the increase in their
173 electrical conductivity as compared to that of the α -Al₂O₃-doped samples. At
174 1173K, the highest power factor of $\sim 8.31 \times 10^{-4} \text{Wm}^{-1}\text{K}^{-2}$ measured in this study is
175 comparable to the value of $\sim 8 - 15 \times 10^{-4} \text{Wm}^{-1}\text{K}^{-2}$ reported by Ohtaki et al [1] and
176 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.

177 The dimensionless figure of merit, ZT , is given in Fig. 7, showing that the ZT
178 values of γ -1073 and γ -1173 are also higher than those of α -1073 and α -1173. At
179 1173K, the γ -1173 sample with the highest power factor attained a ZT of 0.17,
180 which is about 27% higher than that for the α -Al₂O₃-doped counterpart at the
181 same temperature. The highest ZT value of our sample is on the same order of the
182 one reported by Ohtaki et al [1] at the same temperature. It should be noted here
183 that the higher ZT value ($ZT \sim 0.44$ at 1000 K) reported by Jood et al is mainly
184 due to the suppression in the thermal conductivity of the sample by
185 nanostructuring [2]. Nevertheless, our ZT value is higher than the ones reported
186 by Cai et al [10] and Tanaka et al [16] at the same temperature.

187 We found that the ZnO samples doped with γ -Al₂O₃ showed a better
188 thermoelectric performance compared to those doped with α -Al₂O₃, when
189 calcined at a temperature lower than 1273 K. At a calcination temperature higher
190 than 1273 K, the difference in the thermoelectric properties gradually diminishes
191 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

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

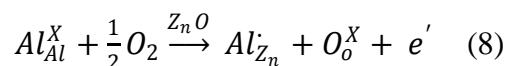
218 According to the experimental data reported by Tsuchida et al [8], the parameters
 219 of A and E_a can be obtained by Arrhenius fitting. A equals $18076 \mu\text{m}^2 \text{min}^{-1}$. E_a for
 220 α -Al₂O₃ and γ -Al₂O₃ equals 4.9 and 2.04 eV, respectively. r_o equals the average
 221 particle size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

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



258
 259 According to the previous investigations by Branson, the diffusion of Al toward
 260 ZnO does not contribute to the formation of ZnAl₂O₄ [7]. His explanation of the
 261 reaction between ZnO and Al₂O₃ did not take the Al diffusion into consideration.
 262 From our experimental results and investigations by other groups who observed
 263 the existence of Al diffusion into ZnO using HRTEM [15], a modified Branson's
 264 schematic diagram of the reaction process is proposed and the details is presented
 265 in Fig. 9. It includes a counter-diffusion between ZnO and Al₂O₃. The formation
 266 of ZnAl₂O₄ is only caused by the diffusion of Zn to Al₂O₃, while the Al
 267 substitution for Zn results from the diffusion of Al into ZnO. The disordered
 268 structure of γ -Al₂O₃ may lead to the disordered product layers of ZnAl₂O₄. The Al
 269 and Zn ions would be easier to diffuse through the disordered product layer. It
 270 promotes both the formation of ZnAl₂O₄ and the substitutions of Al for Zn as
 271 donor impurities in ZnO, thus resulting in enhanced grain boundary pinning by
 272 ZnAl₂O₄ and the observed higher electrical conductivity of the γ -Al₂O₃-doped
 273 ZnO than that of the α -Al₂O₃-doped counterpart.

274 4. Conclusions

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

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333 Figure captions

334 Fig. 1. (a) XRD patterns of α/γ -Al₂O₃-doped ZnO with different calcination temperatures (from
 335 973 to 1273 K). The dotted box magnified as the inset shows the position of the strongest peak
 336 from ZnAl₂O₄. (b) The unit cell volume obtained from the lattice parameter refinement as a
 337 function of the calcination temperature.

338 Fig. 2. SEM photographs of the fracture surfaces of α/γ -Al₂O₃-doped ZnO. (a) γ -973, (b) γ -1073,
 339 (c) α -1073, (d) α -1273, (e) a representative high-magnification SEM image of the ZnAl₂O₄
 340 nanoprecipitates. EDX line scans of Zn, O, and Al K α_1 X-ray peaks obtained along the yellow
 341 arrow are shown in (f).

342 Fig. 3. Temperature dependence of the electrical conductivity of α/γ -Al₂O₃-doped ZnO samples.
 343 The inset shows the electrical conductivity at 1173 K as a function of the calcination temperature.

344 Fig. 4. Temperature dependence of the Seebeck coefficient of α/γ -Al₂O₃-doped ZnO samples. The
 345 inset shows the Seebeck coefficient at 1173 K as a function of the calcination temperature.

346 Fig. 5. Temperature dependence of the thermal conductivity of α/γ -Al₂O₃-doped ZnO samples.
 347 The inset shows the thermal conductivity at 1173 K as a function of the calcination temperature.

348 Fig. 6. Temperature dependence of the power factor of α/γ -Al₂O₃-doped ZnO samples. The inset
 349 shows the power factor at 1173 K as a function of the calcination temperature.

350 Fig. 7. Temperature dependence of ZT of α/γ -Al₂O₃-doped ZnO samples. The inset shows the ZT
 351 values at 1173 K as a function of the calcination temperature.

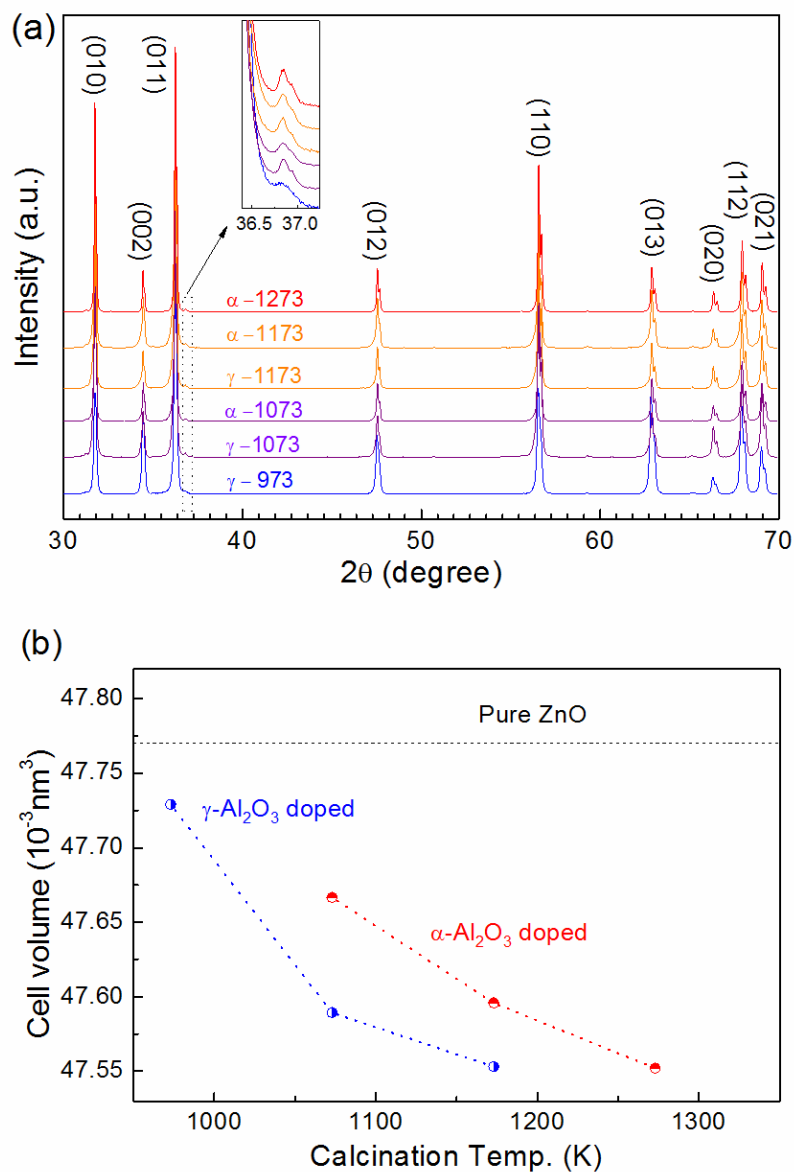
352 Fig.8. (a) The calculated reaction time course as a weight fraction of reacted Al₂O₃ for the
 353 ZnAl₂O₄ formation. (b) The percentage of reaction completed after 1 hour as a function of the
 354 calcination temperature.

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 356 on Branson's investigation.

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359

360 Fig. 1

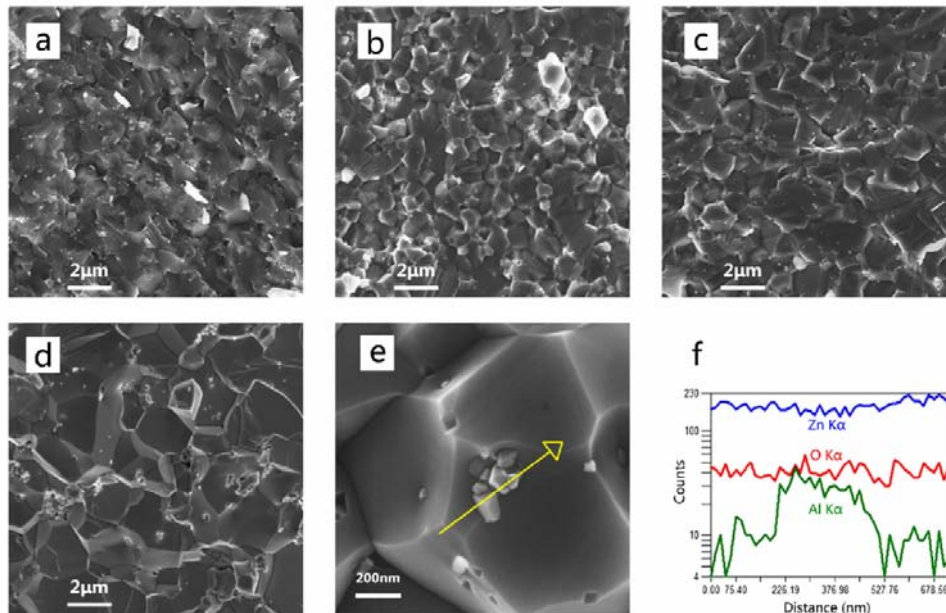


361

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



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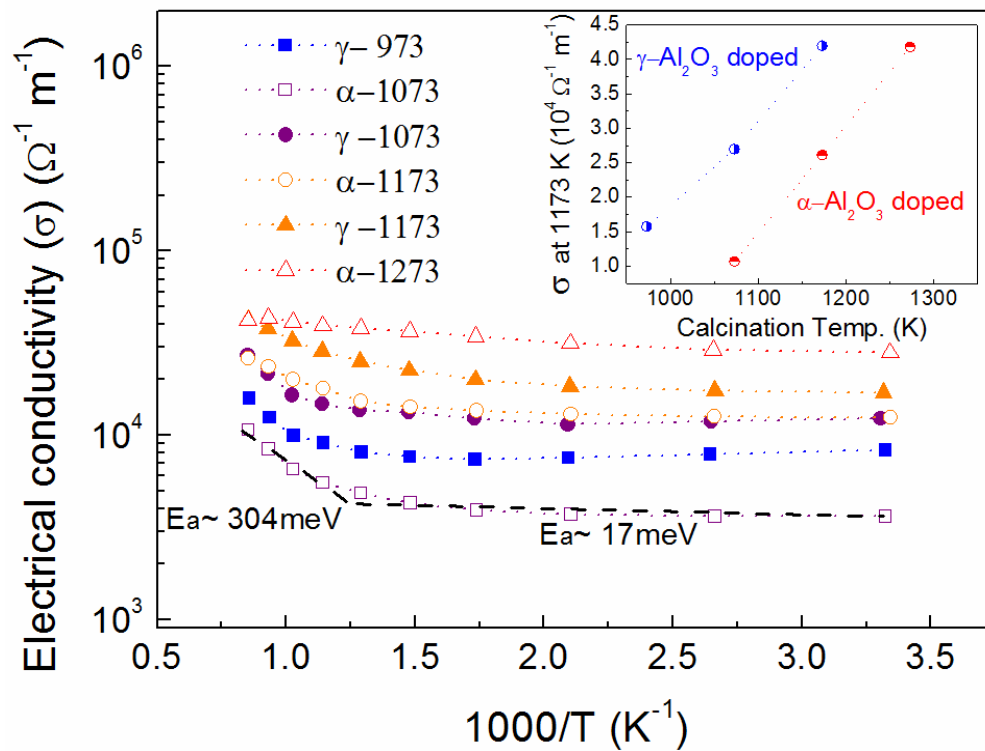
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372 arrow are shown in (f).

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374 Fig. 3



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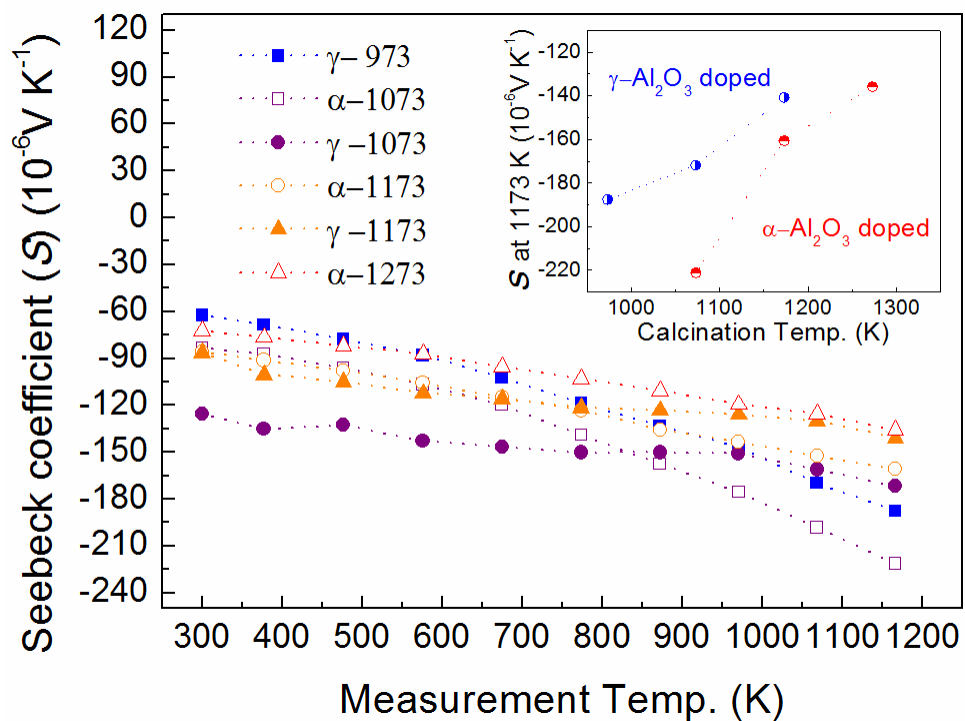
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377 The inset shows the electrical conductivity at 1173 K as a function of the calcination temperature.

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379 Fig. 4



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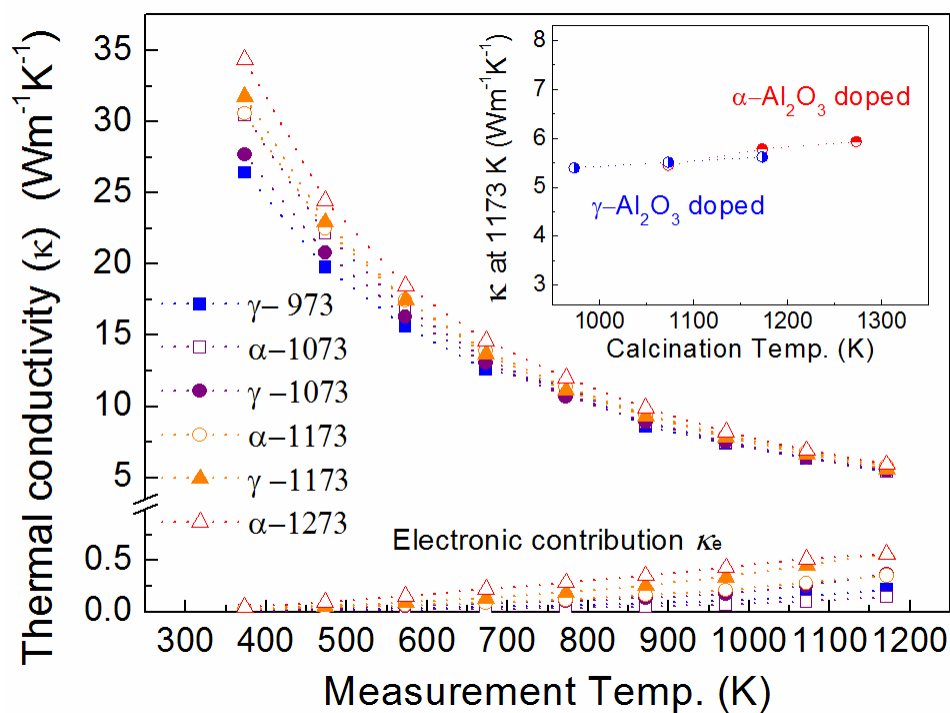
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 382 inset shows the Seebeck coefficient at 1173 K as a function of the calcination temperature.

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384 Fig. 5

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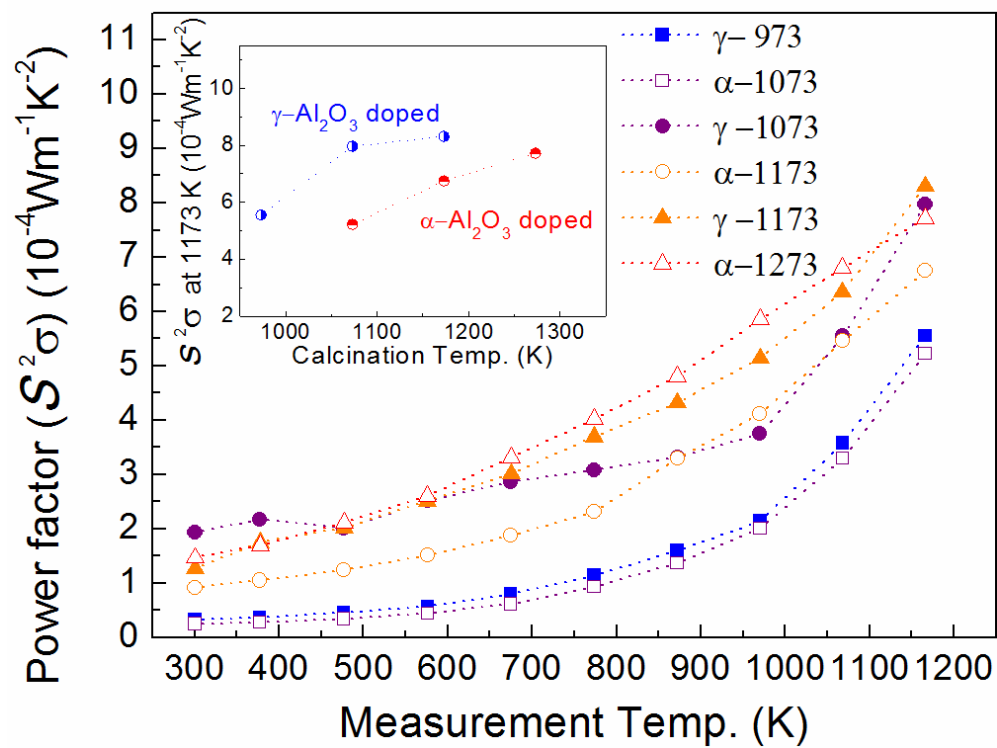
386

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

389

390 Fig. 6



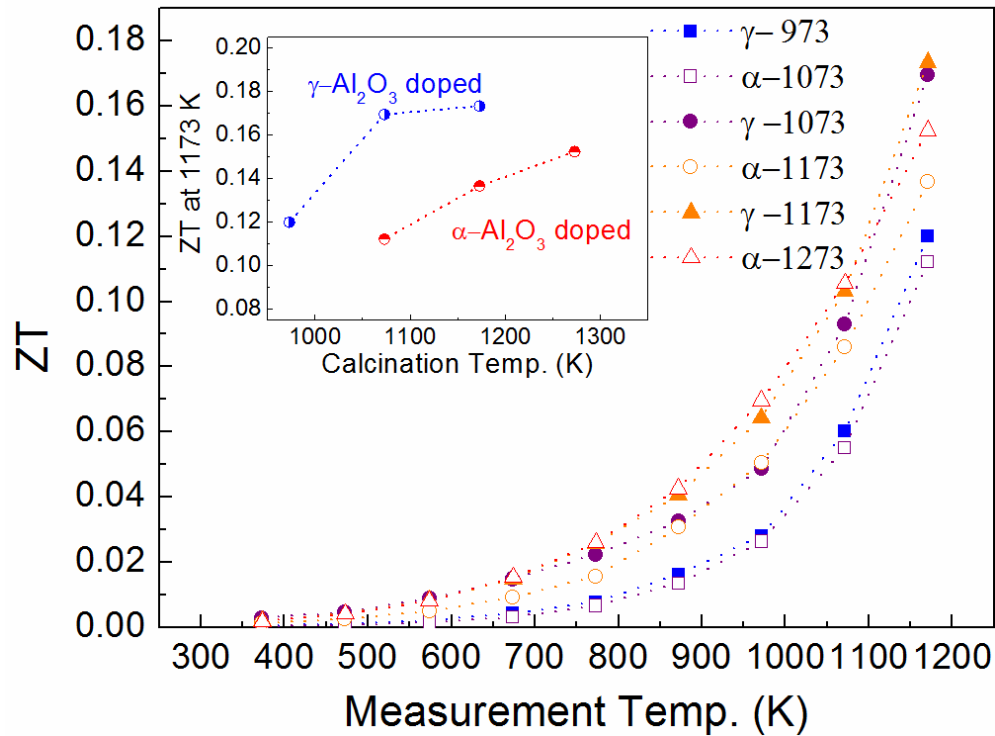
391

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.

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395 Fig. 7



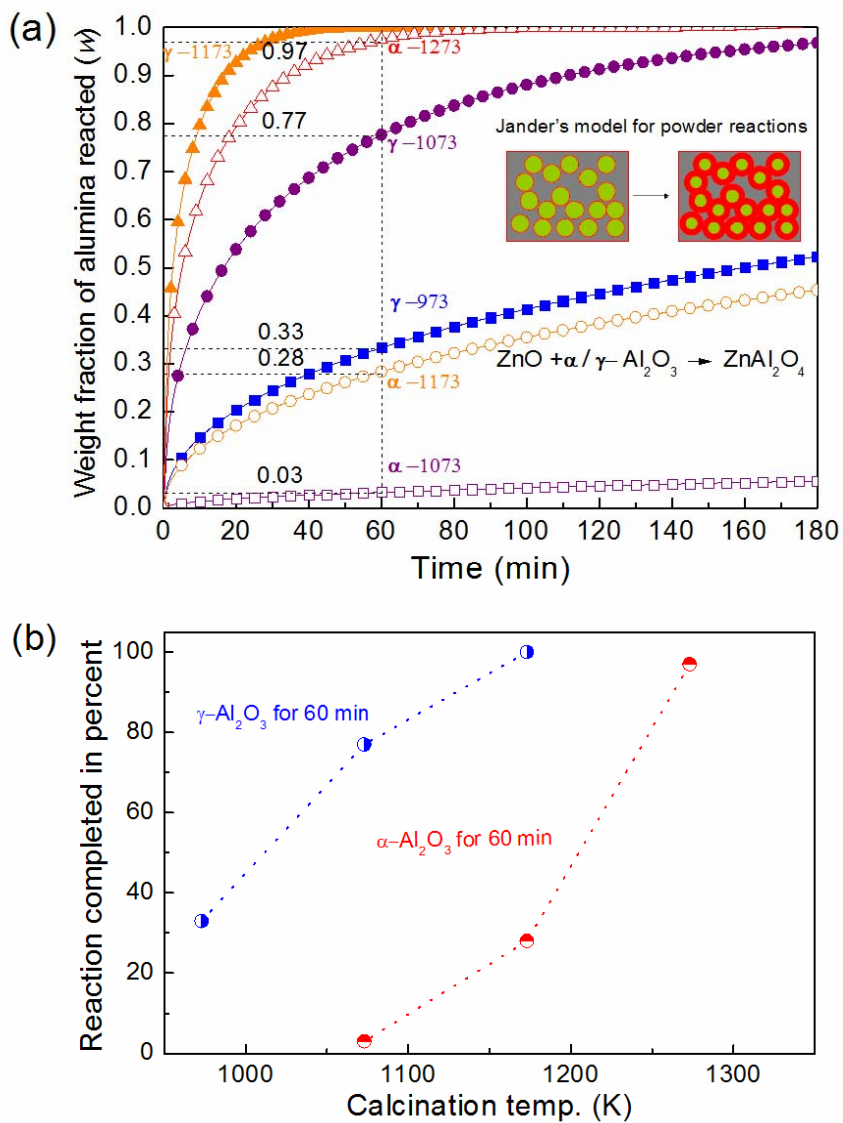
396

397 Fig. 7. Temperature dependence of ZT of α/γ - Al_2O_3 -doped ZnO samples. The inset shows the ZT
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400 Fig. 8



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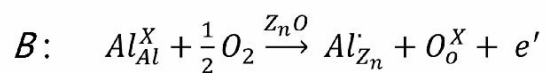
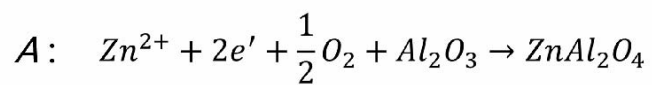
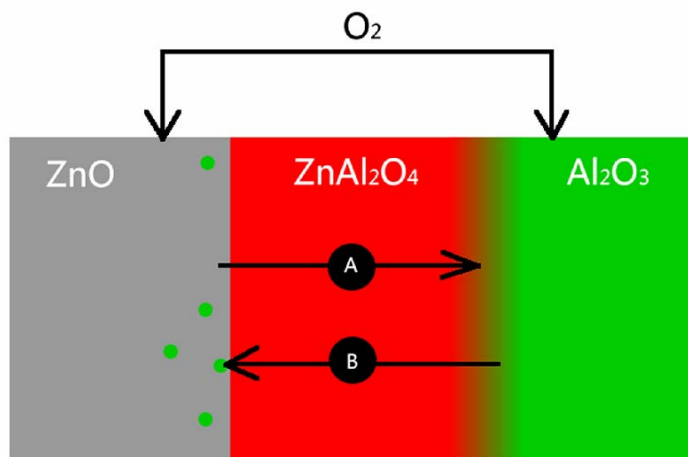
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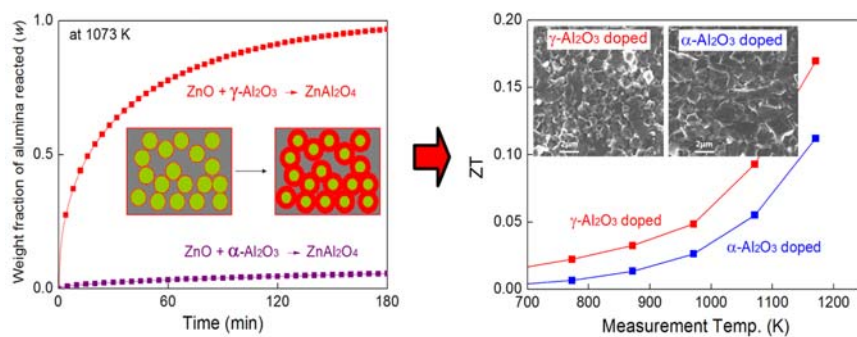
407 Fig. 9



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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.

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