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OPTIMIZATION PARAMETER FOR THERMOELECTRIC PROPERTIES OF ZnO USING RESPONSE SURFACE METHODOLOGY

(Pengoptimuman Parameter Untuk Sifat Termoelektrik ZnO Menggunakan Kaedah Gerak Balas Permukaan)

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Abstract

The effect of Al dopants and sintering temperature on thermoelectric properties of ZnO was studied using the response surface method. The design of experimental work was performed with the response surface method used to determine the significant level of factors which are sintering temperature in the range of 800 – 1000 °C and Al dopants in the range of 0 – 4 wt.%. The thermoelectric properties of Al-doped ZnO were enhanced with increasing Al dopants and slightly decreased when increasing sintering temperature. Additional phase $ZnAl_2O_4$ was detected for 3 wt.% and 4 wt.% Al-doped ZnO pellets as the sintering temperature increased to 1000 °C. The presence of $ZnAl_2O_4$ phase slightly decreased the electrical conductivity compared to single ZnO phase samples. The optimum parameter values for this study was Al dopant (4 wt.%) and sintering temperature (800 °C). The effect of Al doping to the band structure of ZnO was studied using first-principles based on density functional theory (DFT). The calculated band structure of ZnO and Al doped ZnO shows that ZnO is a direct band gap semiconductor. The calculated band gap of ZnO (0.749 eV) become smaller with the concentration of Al doping increased to 4 wt.% (0.551 eV). The trend of the calculated band gap of Al-doped ZnO was in agreement with the electrical conductivity test results which increased with increasing Al content. However, it must be noted that the software predictions do not take into account the presence of additional $ZnAl_2O_4$ phases. The presence of these extra phases may lead to even lower electrical conductivity.

Keywords: Al-doped ZnO, response surface method, sintering temperature, thermoelectric, electronic band structure

Abstrak

Kesan Al dop dan suhu pembakaran ke atas termoelektrik ZnO dikaji dengan menggunakan kaedah gerak balas permukaan. Reka bentuk kerja eksperimen telah dilakukan dengan kaedah gerak balas permukaan untuk menentukan aras signifikan suhu pembakaran pada julat 800 – 1000 °C dan Al dop dalam lingkungan 0 – 4% berat. Sifat – sifat termoelektrik Al-dop ZnO telah dipertingkatkan dengan peningkatan Al dop dan pensinteran suhu. Fasa tambahan $ZnAl_2O_4$ dikesan bagi 3% berat dan 4% berat Al-dop ZnO bila suhu pembakaran meningkat daripada 800 °C hingga 1000 °C. Kekonduksian elektrik menurun dengan kehadiran fasa $ZnAl_2O_4$ berbanding sampel fasa ZnO tunggal. Nilai – nilai parameter optimum untuk kajian ini adalah Al pendopan (4% berat) dan suhu pensinteran (800 °C). Kesan Al doping kepada struktur jalur ZnO dikaji menggunakan prinsip pertama berdasarkan teori fungsi ketumpatan. Struktur jalur yang dikira pada ZnO dan Al dop ZnO menunjukkan bahawa ZnO adalah semikonduktor jurang jalur terus. Dengan Al dop, jurang jalur ZnO (0.749 eV) menjadi lebih kecil dengan peningkatan kepekatan Al dop pada 4 wt.% (0.551 eV). Trend jurang jalur yang dikira pada ZnO Al-didopkan adalah selari dengan keputusan ujian kekonduksian elektrik yang meningkat dengan peningkatan kandungan Al. Walau bagaimanapun, ia perlu diambil perhatian bahawa ramalan perisian tidak mengambil kira kehadiran fasa $ZnAl_2O_4$ tambahan. Kehadiran kedua – fasa tambahan boleh membawa kepada kekonduksian elektrik yang lebih rendah.

Kata kunci: Al dop ZnO, kaedah gerak balas permukaan, suhu pembakaran, termoelektrik, struktur jalur elektronik

Introduction

Thermoelectric materials could potentially convert heat into electricity through thermoelectric power [1]. The efficiency of energy conversion depends on the thermoelectric figure of merit of the material. Based on the figure of merit, these materials must have the unique combination of high electrical conductivity, high Seebeck coefficient and low thermal conductivity [2]. Seebeck coefficient (S) of a material is the voltage generated between two points in the material per unit temperature difference between these points [3].

Zinc oxide (ZnO) is an II-VI compound semiconductor with a wide direct band gap at room temperature [4]. It is a widely used material in various application such as gas sensors, varistors, UV resistive coatings, piezoelectric devices, surface acoustic wave devices and transparent conductive oxide electrodes [5,6]. The main drawback of ZnO as thermoelectric materials is due to the low electrical conductivity at room temperature. The electrical conductivity can be increased by special heat treatment and doping of specific impurities into the crystal lattice. In the hexagonal close packed lattice of the ZnO wurtzite structure, half of the tetrahedral holes and all of the octahedral holes are empty, providing further possible dopant sites [7]. A dopant ion introduced to modify the electronic properties of a material needs to be incorporated into the crystal structure of the host material (either in lattice sites or interstitially). ZnO can even be made to exhibit metallic conductivity as for transparent electrode similar to Indium tin oxide glass. In general, 0.5 – 1% addition of trivalent cations such as aluminium (Al) and chromium (Cr) decrease the resistivity of ZnO approximately 10 orders of magnitude [8]. Jimenez-Gonzalez et al. [9] explains the increase in the conductivity of ZnO when Al is introduced as a dopant, in terms of donor behaviour from Al. Al has one valence electron more than Zn, substitution of Al for the Zn atom or Al occupation of the interstitial sites increases the concentration of charge carriers present in the material.

The properties of ZnO are related to the composition and phase formation. The conductivity properties of ZnO can be tailored by controlling the deviation from stoichiometry and doping [10]. Therefore, it is necessarily to understand the effect of the individual dopant element to the electrical properties and phase formation of ZnO. In this work, the effect of Al dopant (0 – 4 wt.%) and sintering temperature (800 – 1000 ^{o}C) on the thermoelectric properties were studied using the response surface methodology. The band structure of ZnO with different Al contents are calculated by first principles method based on Density Functional Theory (DFT) as a comparison for the electrical conductivity.

Materials and Methods

Chemical and reagent

Analytical grade ZnO powder and Al_2O_3 powder were used as the starting materials for the preparation of pellet samples. The properties of ZnO and Al_2O_3 were shown in Table 1.

Table 1. Properties of ZnO, Al_2O_3, Fe_2O_3 and CuO (HmbG Chemicals)

Properties	Zinc oxide	Alumina
Molecular formula	ZnO	Al_2O_3
Molar mass, g/mol	81.408	375.134
Appearance	white solid	white solid
Density, g/cm^3	5.606	3.95 – 4.1

Experimental procedure

Appropriate amounts of ZnO and Al_2O_3 powder were mixed using the solid state method to prepare 0, 1, 2, 3 and 4 wt.% Al-doped ZnO. The samples were shaped into pellets of 5 mm of thickness and 15 mm in diameter. All

samples were compacted using a cold hydraulic press machine at 75MPa for 10min. The green compact was sintered in furnace (Model HT4-1600-SIC) at different sintering temperature 800 °C, 900 °C and 1000 °C for 4 hours with heating rate of 10 °C/min. The synthesized samples were characterized by X-ray diffraction analysis (Shimadzu XRD 2000). The electrical conductivity of the samples was determined by the two-probe method. The current voltage measurements were carried out using a Keithley's source measure unit (Model SMU 236). The thermal conductivity of the samples was determined based on Fourier's law. The Seebeck coefficient was measured by using differential method [11] at room temperature.

Response surface methodology

Response surface methodology is a statistical method used to improve and optimize process. The response surface methodology has the advantages to evaluate multiple processing parameters and reduced the number of experimental trials. The experimental results were evaluated by the dependent variables of thermoelectric efficiency using Design Expert 8 [12] with surface response model. The results are obtained with the experimental design that was aimed at identifying the best levels of the Al doping (0 – 4 wt.%) and sintering temperature (800 – 1000 °C). The analysis of variance (ANOVA) is a statistical technique for the purpose of testing hypotheses on the parameters of the model. A 3-factor, 3-level factorial Box–Behnken design (BBD) was employed to investigate the effects of selected variables. BBD which is a widely used form of response surface methodology, specially made to require only 3 levels, coded as –1, 0, and +1. BBD is an independent, rotatable or nearly rotatable quadratic design (contains no embedded factorial or fractional factorial design) in which the treatment combinations are at the midpoints of the edges of the process space and at the centre.

Computational method

The ABINIT program was used to perform the band structure calculations. ABINIT is an open source program that used to compute band structure and ground state properties. The band structures of Al doped ZnO was calculated based on the DFT Kohn-Sham equations with GW computations. The GW method is a Green function technique that obtained the electron self-energy and provides an accurate determination of the quasiparticle excitation energies [13]. The k-point parameter was 3 x 3 x 1 Monkhorst-Pack. The cut off energy was set to be 816 eV (30 hartree). The ideal ZnO has a wurtzite structure at normal temperatures and pressures. The primitive cell parameters for ideal ZnO were determined as α = 3.2005 Å, c/α = 1.6131 and u = 0.3792. The parameters used in ABINIT were optimized with a convergence criterion 0.01 eV to calculate self-energy for the band gap.

Results and Discussion

XRD analysis

Based on Figure 1(a), all the samples peaks for 0, 1, 2, 3 and 4 wt.% Al-doped ZnO were identified as the plane reflection for wurtzite phase of ZnO according to the JCPDS data file (No. 36-1451). The XRD pattern of Al-doped ZnO sintered at 900 °C was indicated in Figure 1(b). Based on the test results, all the peaks for 0, 1, 2, 3 and 4 wt.% Al-doped ZnO matched the JCPDS data file (No.36-1451) as the plane reflection for wurtzite phase of ZnO. There was additional phase $ZnAl_2O_4$ that matched the JCPDS data file (No.05-0669) detected for 4 wt.% Al-doped ZnO sintered at 900 °C. From the test results show in Figure 1(c), additional phase $ZnAl_2O_4$ was detected for 3 wt.% and 4 wt.% Al-doped ZnO with the sintering temperature increased to 1000 °C. The existence of secondary phase $ZnAl_2O_4$ may reduce the electrical conductivity of the sample [14].

Electrical conductivity

Based on the analysis of variance (ANOVA) for electrical conductivity as shown in Table 2, the Model F-value of 404.80 implies the model was significant. The Prob > F values of less than 0.05 may indicate that Al dopants and sintering temperature have significant effects on the electrical conductivity of the samples.

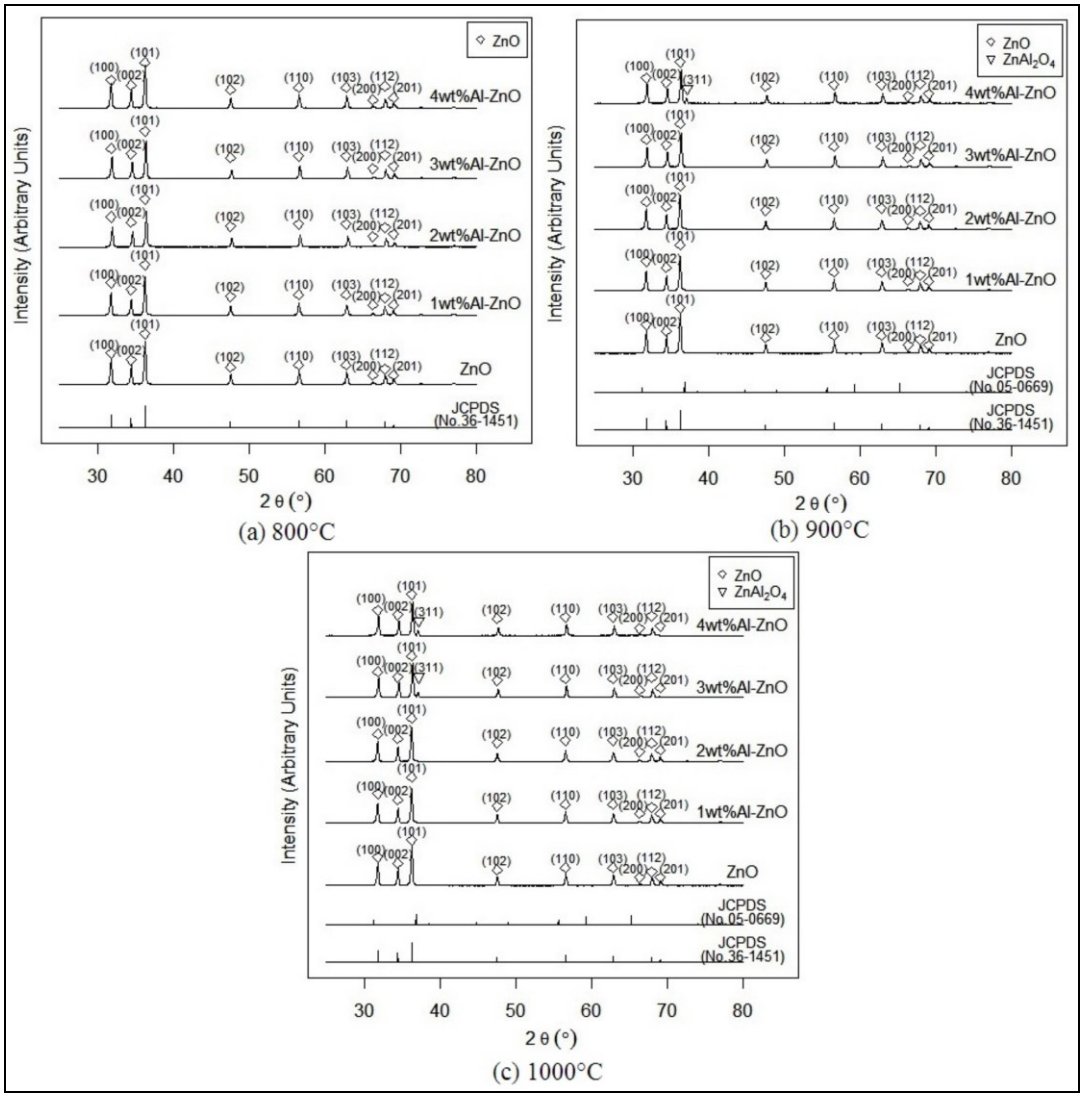

Figure 1. XRD pattern of Al-doped ZnO sintered at (a) 800 °C (b) 900 °C (c) 1000 °C

Table 2. Analysis of variance for electrical conductivity

Source	**Sum of Squares**	**Df**	**Mean Square**	**F value**	**p-value Prob > F**
Model	8219.08	5	1643.82	404.80	< 0.0001
A-Al dopants	7360.83	1	7360.83	1812.63	< 0.0001
B-Sintering temperature	14.18	1	14.18	3.49	0.0245
AB	12.31	1	12.31	3.03	0.1157
A^2	831.35	1	831.35	204.72	< 0.0001
B^2	0.41	1	0.41	0.100	0.7591
Residual	36.55	9	4.06		
Cor Total	8255.62	14			

Figure 2 show the 3D plot for electrical conductivity profile in accordance to the response surface model. The highest peak electrical conductivity for ZnO was achieved with 4wt.% Al dopants sintered at temperature 800 °C. Based on results shown in Figure 2, increasing the concentration of Al dopant caused a significant increase in the electrical conductivity. This might due to the Al dissolved in the ZnO crystal lattice acts as donor [15]. For example, the electrical conductivity of bulk pellets was increased significantly from 9.95 S/cm (pure ZnO) to 37.39 S/cm, 59.38 S/cm, 69.26 S/cm and 71.49 S/cm as the dopant increased to 1, 2, 3 and 4 wt.% respectively. The electrical conductivity for 4 wt.% Al-doped ZnO sintered in air at 1000 °C (70.98 S/cm) and 900 °C (71.49 S/cm) were slightly lower compared to 800 °C (71.87 S/cm). This might due to the existence of $ZnAl_2O_4$ phase as shown in Figure 1. The $ZnAl_2O_4$ phase believed to induce oxygen vacancies that lead to low conductivity. The formation of this phase may cause the resistivity increase in the samples [16].

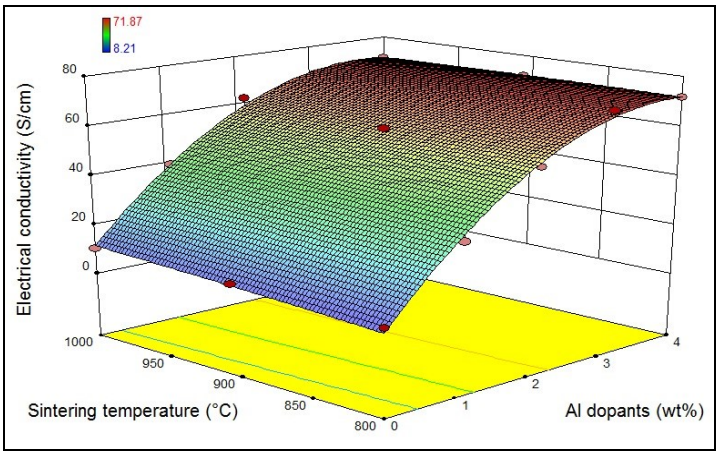

Figure 2. 3D response surface plot for electrical conductivity of Al-doped ZnO

Band structure

The electronic band structure for ZnO calculated using DFT was shown in Figure 3. The band structure shows that ZnO is direct band gap material with the valence band maximum (VBM) and the conduction band minimum (CBM) at G. The calculated band gap at point G is 0.749 eV for ZnO. Low band gap might be due to the lower exchange correlation between electrons made by the DFT-GW function.

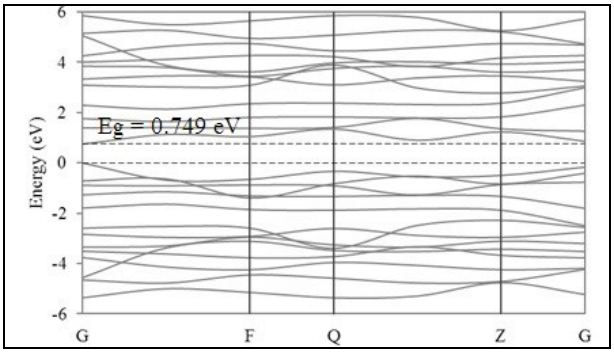

Figure 3. Electronic band structure of pure ZnO

Figure 4(a)-(d) shows the calculated band structure of 1 wt.% Al-ZnO, 2 wt.% Al-ZnO, 3 wt.% Al-ZnO and 4 wt.% Al-ZnO respectively, the corresponding band gap are 0.684 eV, 0.619 eV, 0.557 eV and 0.551eV. The band gap values of Al doped ZnO are smaller than pure ZnO shown in Figure 3. The band gap of Al doped ZnO becomes smaller with increasing Al doping content. This may due to increase of carrier concentration and enhancement of conduction [19]. As shown from Figure 4(a)-(d), The CBM and VBM are all located in the G point, it indicated that Al doped ZnO is a direct band gap semiconductor. The electrical conductivity test results were similar to the calculated band gap. The band gap becomes smaller with the amounts of Al doping increased that resulting an increase in electrical conductivity. This emphasized that a reduction of the band gap would increase the intrinsic (without defects) conductivity of ZnO. It shifts the intrinsic defect states to energies inside the conduction band.

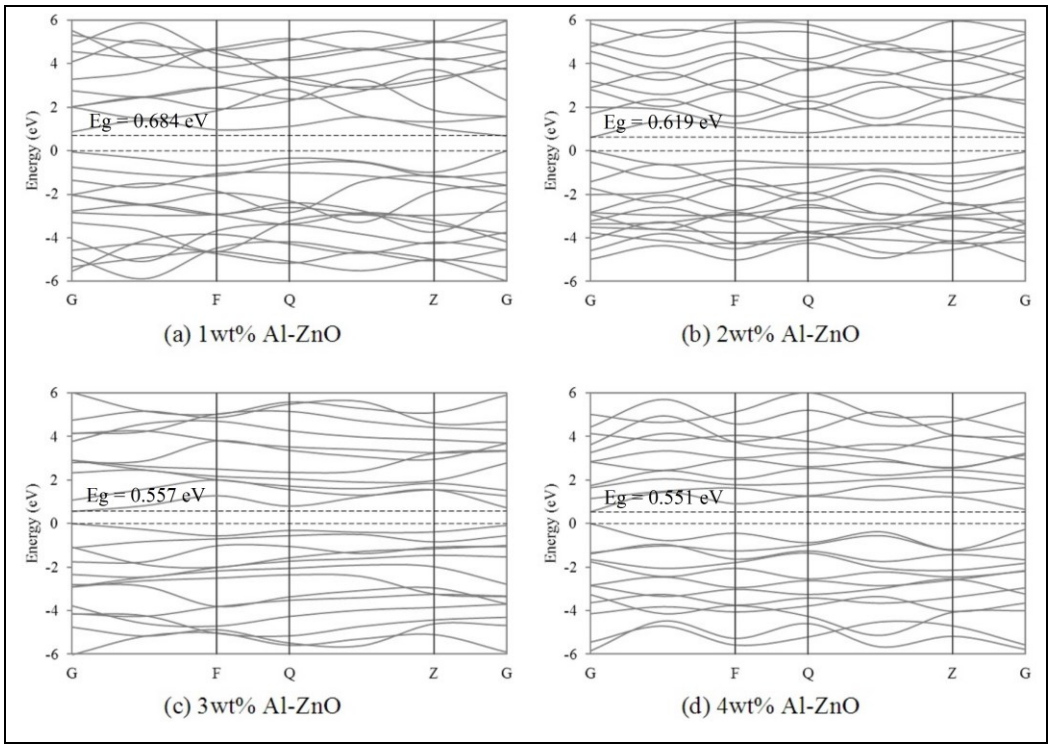

Figure 4. Electronic band structure of Al doped ZnO

Thermal conductivity

Table 3 show the analysis of variance (ANOVA) output used to estimate the variation due to each factor. The Model F-value of 51477.35 implies the model was significant. Values of "Prob > F" less than 0.05 indicate the model terms are significant. The ANOVA indicates that changing the sintering temperature and Al dopants may have a significant effect on the thermal conductivity of the samples.

The highest peak thermal conductivity for ZnO was achieved for pure ZnO sintered at 800°C. Based on results shown in Figure 5, increasing the amount of Al dopants caused a decrease in the thermal conductivity of the samples. The thermal conductivity of ZnO was 34.59 W/mK reduced to 33.21 W/mK, 31.82 W/mK, 30.44 W/mK and 29.05 W/mK with the Al doping increased to 1, 2, 3 and 4 wt% respectively. The reduction of thermal conductivity might due to the Al dopant suppress the lattice thermal conductivity of ZnO materials [20]. The thermal conductivity of the ZnO pellets decreased slightly when increasing the amount of Al dopants. The wurtzite ZnO has a high intrinsic thermal conductivity due to its strong covalent bonding and light atoms. The decrease in the thermal conductivity might be due to a phonon scattering caused by increased ZnO crystal lattice disorder when

Al dopants were added.

Table 3. Analysis of variance for thermal conductivity

Source	Sum of Squares	Df	Mean Square	F value	p-value Prob > F
Model	83.85	5	16.77	51477.35	< 0.0001
A-Al dopants	56.42	1	56.42	1.732E+005	< 0.0001
B-Sintering temperature	26.67	1	26.67	81852.09	< 0.0001
AB	0.099	1	0.099	305.12	< 0.0001
A^2	9.524E-006	1	9.524E-006	0.029	0.8680
B^2	0.67	1	0.67	2062.67	< 0.0001
Residual	2.932E-003	9	3.258E-004		
Cor Total	83.86	14			

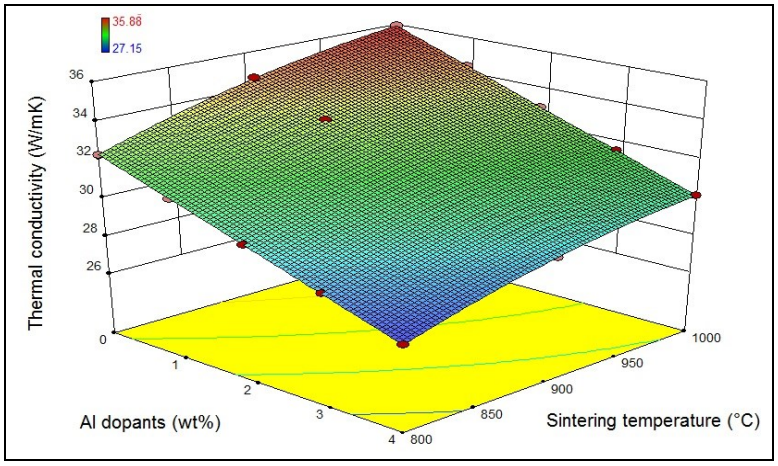

Figure 5. 3D response surface plot for thermal conductivity of Al-doped ZnO

Seebeck coefficient

Based on the analysis of variance for Seebeck coefficient as shown in Table 4, the Model F-value of 370.54 implies the model was significant. The Prob > F values below 0.05 may indicate that the sintering temperature and Al dopants have a significant effect on the Seebeck coefficient.

Figure 6 show a 3D plot curvilinear profile in accordance to the response surface model for the Seebeck coefficient. The highest peak Seebeck coefficient for ZnO was achieved for pure ZnO sintered at 1000 °C. Based on results shown in Figure 6, an increase in the Al doping concentration caused a decrease in the Seebeck coefficient of the bulk pellets. This might due to the Al dissolved in the ZnO crystal lattice acts as donor that improved the electrical conductivity and carrier concentration [21]. The negative sign of the Seebeck values was used to indicate the samples were n-type semiconductors. The magnitude of Seebeck coefficient for ZnO was 50.22 μV/K decreased to 49.22 μV/K, 48.71 μV/K, 48.21 μV/K and 47.95 μV/K with the Al dopant increased to 1, 2, 3 and 4 wt.% respectively.

Table 4. Analysis of variances for Seebeck coefficient

Source	Sum of Squares	Df	Mean Square	F value	p-value Prob > F
Model	16.48	5	3.30	370.54	< 0.0001
A-Al dopants	10.33	1	10.33	1160.46	< 0.0001
B-Sintering temperature	5.63	1	5.63	632.19	< 0.0001
AB	4.805E-003	1	4.805E-003	0.54	0.4811
A^2	0.40	1	0.40	44.54	< 0.0001
B^2	0.13	1	0.13	14.99	0.0038
Residual	0.080	9	8.898E-003		
Cor Total	16.56	14			

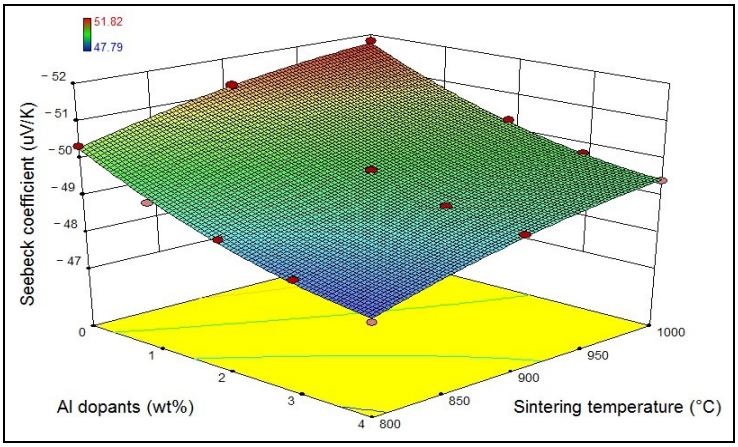

Figure 6. 3D response surface plot for Seebeck coefficient of Al-doped ZnO

Thermoelectric figure of merit

The thermoelectric figure of merit calculated from the measured values of electrical conductivity, Seebeck coefficient and thermal conductivity was shown in Figure 7. Higher figure of merit values (0.61) was observed for 4 wt.% Al-doped ZnO pellet sintered at 800 °C. The figure of merit for Al-doped ZnO was improved by doping Al. The figure of merit for 4 wt.% Al-doped ZnO sintered at 800 $^{\circ}$C was higher (Z ~ 0.58 x10^{-6}) due to high electrical conductivity and low thermal conductivity was obtained when increasing Al. The figure of merit for Al-doped ZnO (Al > 3 wt.%) was decreased when increasing sintering temperature. This was due to the formation of $ZnAl_2O_4$ phase at higher sintering temperature that lead to the reduction of electrical conductivity [22]. The presence of $ZnAl_2O_4$ phase was observed to reduce the figure of merit compared to single ZnO phase samples. This indicated the additional $ZnAl_2O_4$ phases had a deleterious effect on the thermoelectric properties.

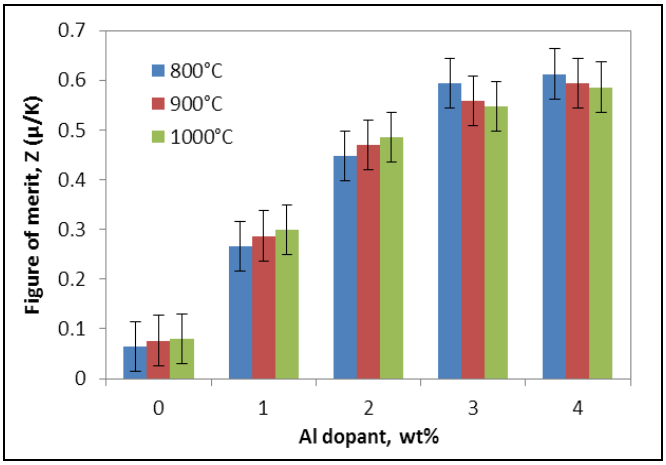

Figure 7. Figure of merit of Al-doped ZnO

Conclusion

Thermoelectric properties of ZnO were improved with increasing the amount of Al dopants. The thermoelectric figure of merit for 4 wt.% Al-doped ZnO (0.61) yielding a 10 times enhancement compared to the pure ZnO (0.06). The electrical conductivity of Al-doped ZnO was increased with increasing the amount of Al dopants. The Seebeck coefficient and thermal conductivity were decreased for Al-doped ZnO with increasing the amount of Al dopants. Thermoelectric properties of Al-doped ZnO were decreased with increasing the sintering temperature due to the additional phase $ZnAl_2O_4$. The thermoelectric figure of merit for 4 wt.% Al-doped ZnO (0.61) with lower sintering temperature (800 °C) was higher compared to the 4 wt.% Al-doped ZnO (0.58) sintered at higher temperature (1000 °C). Based on the analysis of variance, the sintering temperature and Al dopants have a significant effect to the thermoelectric properties of Al doped ZnO. Based on the response surface, the optimum values for this study were Al dopant (4 wt.%) and sintering temperature (800 °C). By using the first principles method based on DFT, the band structure of ZnO and Al doped ZnO were calculated. The band structure calculation of Al doped ZnO was investigated to provide a reference values for the electrical conductivity. Based on the DFT calculation, ZnO is a direct band gap. The band gap getting narrow as the concentration of Al doping increased from 1wt.% (0.684 eV) to 4 wt.% (0.551 eV) compare to pure ZnO (0.749 eV).

Acknowledgement

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