Available online at www.sciencedirect.com

ScienceDirect

Materials Today: Proceedings 5 (2018) 13971–13978

materialstoday: PROCEEDINGS

www.materialstoday.com/proceedings

SACT 2016

Synthesis of $Zn_{0.96}Al_{0.04}O$ thermoelectric material for fabrication of thermoelectric module and thermoelectric generator

S. Chanprateep[a] and C. Ruttanapun[a,*]

[a]*Department of Physics, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang, Ladkrabang, Bangkok 10520, Thailand*

Abstract

The main objective of this work is aim to synthesize $Zn_{0.96}Al_{0.04}O$ thermoelectric materials for fabricating thermoelectric modules and inventing thermoelectric generator. The $Zn_{0.96}Al_{0.04}O$ sample was prepared by a conventional solid state reaction method. The formation of structure was proved by X-ray diffraction and the thermoelectric properties were measured. The results presented that the $Zn_{0.96}Al_{0.04}O$ displayed thermoelectric materials and showed the thermoelectric properties as higher than that of ZnO based. The $Zn_{0.96}Al_{0.04}O$ thermoelectric modules displayed the electric power was increased with number of module, large temperature difference and operation at high temperature. The $Zn_{0.96}Al_{0.04}O$ thermoelectric generator showed high performance for electric generator at high temperature. The sixteen $Zn_{0.96}Al_{0.04}O$ legs thermoelectric generator can generate electric power 1.4 mW at 800 in ΔT = 600 °C. Thus, the $Zn_{0.96}Al_{0.04}O$ thermoelectric material can be used for application of thermoelectric generator at high temperature.

Selection and/or Peer-review under responsibility of SACT 2016.

Keywords: thermoelectric; $Zn_{0.96}Al_{0.04}O$; thermoelectric module; thermoelectric generator

1. Introduction

Thermoelectric generator (TEG) was a device, which generated electrical energy directly from heat or temperature difference by phenomenon of thermoelectric effect. The efficiency of thermoelectric material is governed by the dimensionless Fig. of merit (ZT) ,which is the formula of $ZT = S^2\sigma T/\kappa$, where S, σ, κ and T are the Seebeck coefficient, the electrical conductivity, the thermal conductivity and the absolute temperature, respectively.

* Corresponding author. Tel.: +66-02-326-4339-53 ext. 285 to 6; fax: +66-02-326-4413.
E-mail address: chesta.ruttanapun@gmail.com, chesta.ru@kmitl.ac.th

The best of thermoelectric properties of thermoelectric materials for the high thermoelectric generator is controlled by value of high Seebeck coefficient, high electrical conductivity and low thermal conductivity. The thermoelectric generator devices are composed of thermoelectric modules and they were the key factor for energy conversion of thermoelectric generator [1]. The thermoelectric modules are invented from using alternating of the *p*-type and *n*-type semiconductor legs connected by metallic plate interconnect.

In the present day, the best thermoelectric materials are Bi_2Te_3 [2], and ZnO. Both Bi_2Te_3 and ZnO were used for many applications of thermoelectric devices. Unfortunately, the Bi_2Te_3 contained a lot of disadvantages such as low melting and very expensive cost. Meanwhile, the ZnO contained a lot of advantage such as high melting point at 1800 °C [3] ,low cost, and non-poisonous. Thus, the ZnO is interesting for thermoelectric material than the Bi_2Te_3 for application of thermoelectric device in high temperature. In addition, the ZnO can be prepared in easy via a conventional solid state reaction method [4] for large amount products. However, the ZnO has displayed the poor *ZT* value of thermoelectric properties.

Therefore, this work aims to improve thermoelectric properties of the ZnO thermoelectric material by doped with Al_2O_3 as formula $Zn_{1-x}Al_xO$. The ZnO and $Zn_{1-x}Al_xO$ were synthesized by solid state reaction method. Both samples were characterized the properties and compared with previous work [1]. In addition, for thermoelectric application in high temperature, the $Zn_{1-x}Al_xO$ bulk sample was used to fabricate thermoelectric module. Then, the $Zn_{1-x}Al_xO$ thermoelectric modules were used to invent thermoelectric device of thermoelectric generator at high temperature. The $Zn_{1-x}Al_xO$ thermoelectric module and thermoelectric generator were measured the electric conversion from heat at high temperature.

2. Experimental

The samples of ZnO and $Zn_{0.96}Al_{0.04}O$ were prepared by conventional solid state reaction method as according to the following equation:

$$2(1-x)ZnO + xAl_2O_3 \rightarrow 2Zn_{(1-x)}Al_xO + \frac{3}{2}O_2 \;\; 2\theta = 10-80 \tag{1}$$

The starting powder of ZnO (≥99%, Ajex Finechem) and Al_2O_3 (≥98%, Sigma Aldrich) was used. The powders were ground for homogenous mixture in A-grade mortar for 30 min. Then, the homogenous powder was calcined in furnace at 600 °C for 1 hr. in air atmosphere. The calcined powder was pressed into pellets of 10 mm diameter at pressure of 3 Mpa. The pelleted samples were sintered in furnace at 1200 °C for 20 hrs. in air atmosphere.

The phase patterns of sintered ZnO and Al-doped ZnO samples was characterized X-ray diffraction (XRD) of the Bruker, D8 Advance with X-ray source $\lambda_{CuK\alpha}$ = 1.5406 Å and was measured in range of $2\theta = 10-80$ degree by 0.02 steps. The morphology of the samples was observed by using a scanning electron microscope (SEM), Evo Ma 10. The density (*d*) of sample was calculated by the formula $d = m/V_m$, where m and V_m are mass and volume of the samples, respectively. The thermoelectric parameters (electric resistivity (ρ), Seebeck coefficient (*S*) and thermal conductivity (κ)) were measured simultaneously in temperature from 50 °C to 500 °C on the pellets (10 mm * 3mm) with carried out in LINSEIS LZT meter instrument. Then, the sintered ZnO and $Zn_{0.96}Al_{0.04}O$ powder was used to invert thermoelectric module. The invention process of thermoelectric module was consisted as following that 1) the calcined powder was cylinder pressed into 10 mm diameter and 17 mm length, 2) the cylinder bulk was sintered at 1200 °C for 20 hrs. in the air atmosphere, and 3) the cylinder bulk was contacted top and bottom electrodes, which were the stainless steel plated for heat resistance at high temperature and high melting point for thermoelectric module. Next, the thermoelectric modules were tested the electric energy conversion from heat by using the high temperature electrical furnace with carried out data (electric voltage (*Vol*), current (*I*) and power (*P*)) with multi-meter (Agilent 34461A Digit Multi-meter). Finally, the thermoelectric generator was inverted by several connections of thermoelectric modules with the energy conversion by using the in-house thermoelectric testing chamber.

3. Results and discussion

The powder X-ray diffraction (XRD) spectrum of the sintered ZnO and $Zn_{0.96}Al_{0.04}O$ samples were shown in Fig. 1. The XRD reference phases of file PDF#890511 for the ZnO phase as wurtzite structure were included for comparison with the phase patterns of the sintered ZnO and $Zn_{0.96}Al_{0.04}O$ samples. The results showed that main XRD phases of the sintered ZnO sample was corresponded to the reference phase of file PDF#890511 of the ZnO phases and of the sintered $Zn_{0.96}Al_{0.04}O$ sample was related with the reference ZnO phase and sintered ZnO phases with tiny secondary phase of $ZnAl_2O_4$ spinel phase. This confirmed that both sintered ZnO and $Zn_{0.96}Al_{0.04}O$ samples formed phase of ZnO structure.

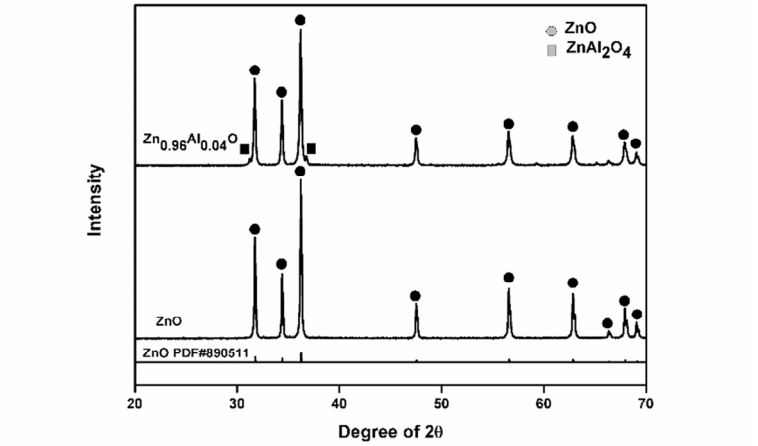


Fig. 1. XRD pattern of sintered ZnO and $Zn_{0.96}Al_{0.04}O$ samples with insertion of the ZnO reference.

The lattice parameter, c/a ratio and volume unit cell were presented in Table 1. The lattice parameters (a,c) and volume unit cell (V) were calculated according to the following equation (2) and (3), respectively.

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2} \tag{2}$$

$$V = \frac{\sqrt{3}}{2} a^2 c \tag{3}$$

The lattice parameters of the sintered ZnO sample were a =3.251Å and c = 5.206 Å as corresponding to the results in the literature [5]. The lattice parameters of the sintered $Zn_{0.96}Al_{0.04}O$ samples were a = 3.249Å, and c = 5.205 Å as closely to the results of the sintered ZnO sample. The results were affected for volume of the sintered $Zn_{0.96}Al_{0.04}O$ sample (37.587 $Å^3$) as smaller than that of the sintered ZnO (37.601 $Å^3$) sample. The result was due to the small ionic radii Al^{3+} (= 0.50 Å) ions substitution for the Zn^{2+} (= 0.83 Å) sites. For the c/a ration, the results displayed that the value of the sintered $Zn_{0.96}Al_{0.04}O$ sample is similar to the sintered ZnO sample as 1.602.

Table 1. The crystal properties of sintered ZnO and $Zn_{0.96}Al_{0.04}O$ samples.

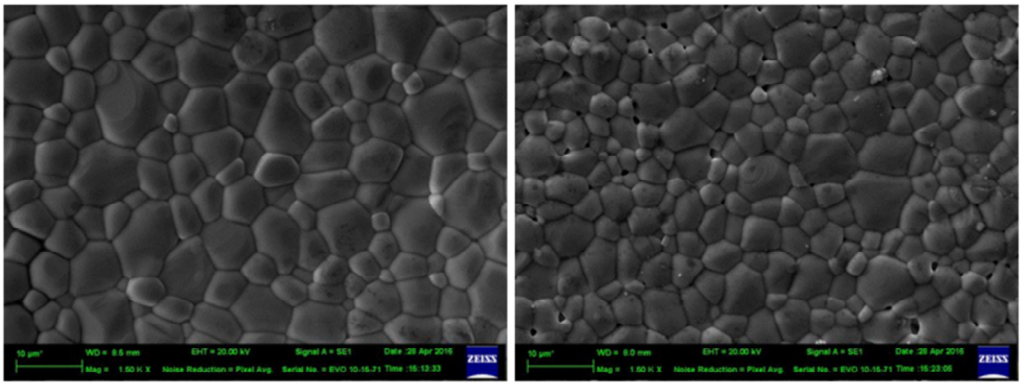
Preparation method	materials	Lattice parameter: a (Å)	Lattice parameter: c (Å)	c/a ratio	Volume unit cell ($Å^3$)	Grain size (μm)	Lattice strain
SSR	ZnO	3.251	5.206	1.602	37.601	9.333	0.107
SSR	$Zn_{0.96}Al_{0.04}O$	3.249	5.205	1.602	37.587	7.636	0.162

The lattice strain value of the sintered ZnO and $Zn_{0.96}Al_{0.04}O$ samples as shown in Table 1 was estimated by using Williamson – Hall equation as following equation:

$$\beta_{hkl}\cos\theta = \frac{K\lambda}{D} + 4\varepsilon\sin\theta \quad (4)$$

where β_{hkl}, D, λ and K were the full width at half maximum (FWHM) intensity of the diffraction peak, the rain size, the wave length of X-ray tube (Cu) and the Scherrer constant, respectively [6]. The results show that the lattice strain of the sintered $Zn_{0.96}Al_{0.04}O$ sample (0.162) was larger than that of the sintered ZnO sample (0.107). This result was affected from the Al atom substitution for the Zn sites of the structure.

Fig. 2 shows the morphology of the sintered ZnO and $Zn_{0.96}Al_{0.04}O$ samples devalued by the scanning electron microscope (SEM). The results shown that the grain size of the sintered ZnO and $Zn_{0.96}Al_{0.04}O$ samples were 9.333 and 7.636 μm, respectively, as displayed in Table 1. The value showed that the grain size of the sintered $Zn_{0.96}Al_{0.04}O$ sample was smaller than that of the sintered ZnO samples. The reducing of grain sized of the $Zn_{0.96}Al_{0.04}O$ sample from the ZnO sample was resulted from the pinning effect from minor phase of tiny impurity $ZnAl_2O_4$ [7-8].



(a) (b)

Fig. 2. The morphology from SEM for (a) ZnO and (b) $Zn_{0.96}Al_{0.04}O$ samples.

From the results of the XRD and SEM image, the results confirmed that the $Zn_{0.96}Al_{0.04}O$ sample as prepared by the solid state reaction method in this work formed the ZnO structure of wurtzite phase. Moreover, the results confirmed the Al atom substitution for Zn sites in the structure. Thus, the sintered $Zn_{0.96}Al_{0.04}O$ sample was investigated thermoelectric propertied (electric resistivity (ρ), Seeback coefficient (S) and thermal conductivity (κ)) for fabrication thermoelectric module. The ρ, S and κ value of the sintered $Zn_{0.96}Al_{0.04}O$ sample was measured simultaneously with temperature from 50 °C to 500 °C. The sample density (d) of the $Zn_{0.96}Al_{0.04}O$ sample were measured for calculation of the κ value vial the relationship $\kappa = C_p*D*d$, where D was thermal diffusivity, d was sample density and C_p was heat capacity. The density of sintered $Zn_{0.96}Al_{0.04}O$ sample was 4.46 g/cm^3 as representing 80% of the theoretical density. The power factor (PF) of the sample was calculated by using the equation of $PF=S^2\sigma$, where $\sigma=1/\rho$ and σ was electrical conductivity and the dimension less Fig. of Merit (ZT) of the sample was calculated via the relation of $ZT= S^2\sigma/\kappa$.

Fig. 3 shows the measured thermoelectric properties (σ) of the $Zn_{0.96}Al_{0.04}O$ sample with comparing to results of previous works. Fig. 3(a) shows the electrical conductivity of the sintered $Zn_{0.96}Al_{0.04}O$ sample as comparing to results of previous works. The results showed that σ of the $Zn_{0.96}Al_{0.04}O$ sample were higher than that of the ZnO results from the previous works. The large σ value of the $Zn_{0.96}Al_{0.04}O$ sample was due to the Al^{3+} cations substituted for the Zn^{2+} sites causing to increase electron concentration of the system. Fig. 3(b) shows the S of the sintered $Zn_{0.96}Al_{0.04}O$ sample as comparing to results of previous works of the ZnO results. The S value of the $Zn_{0.96}Al_{0.04}O$ sample displayed minus sign over the whole temperature range of value as indicating of n-type conductor from major conductivity carriers as electrons. The S value of the $Zn_{0.96}Al_{0.04}O$ sample was increased with increasing temperature, as playing semiconductor behavior [9]. The results displayed that the S value of the sintered

$Zn_{0.96}Al_{0.04}O$ sample was larger than of the *S* value of previous works of the ZnO results. Fig. 3(c) shows *PF* value of the sintered $Zn_{0.96}Al_{0.04}O$ sample as comparing to results of previous works of the ZnO results. The results showed the *PF* value of the $Zn_{0.96}Al_{0.04}O$ sample as higher than that of previous works of the ZnO results. Fig. 3(d) shows thermal conductivity (κ) of the sintered $Zn_{0.96}Al_{0.04}O$ sample as comparing to results of previous works the ZnO results. The results showed the κ value of the $Zn_{0.96}Al_{0.04}O$ sample decrease with increasing temperature as similar to the previous work the ZnO results [10-13]. The results showed the κ value of the $Zn_{0.96}Al_{0.04}O$ sample as lower than that of previous works of the ZnO results. This resulted was affected from the Al-doped for ZnO structure. Fig. 3(e) shows the *ZT* value of the $Zn_{0.96}Al_{0.04}O$ sample as comparing to results of previous works the ZnO results. The results of *ZT* value of sample was still tended to increase with increasing temperature and was higher than that of previous works of the ZnO results. For highest thermoelectric propertied in this work, the σ, *S* and *PF* were 2.02 W/mK ,-151.07 μV/K and $1.51x10^{-4}$ W/mK^2 at 500 ° C, respectively. In addition, the maximum *ZT* of the $Zn_{0.96}Al_{0.04}O$ sample of this work was appeared 0.06 at 500 °C. This result was affected from the Al^{3+} ions substitution for the Zn^{2+} sites of the ZnO structure.

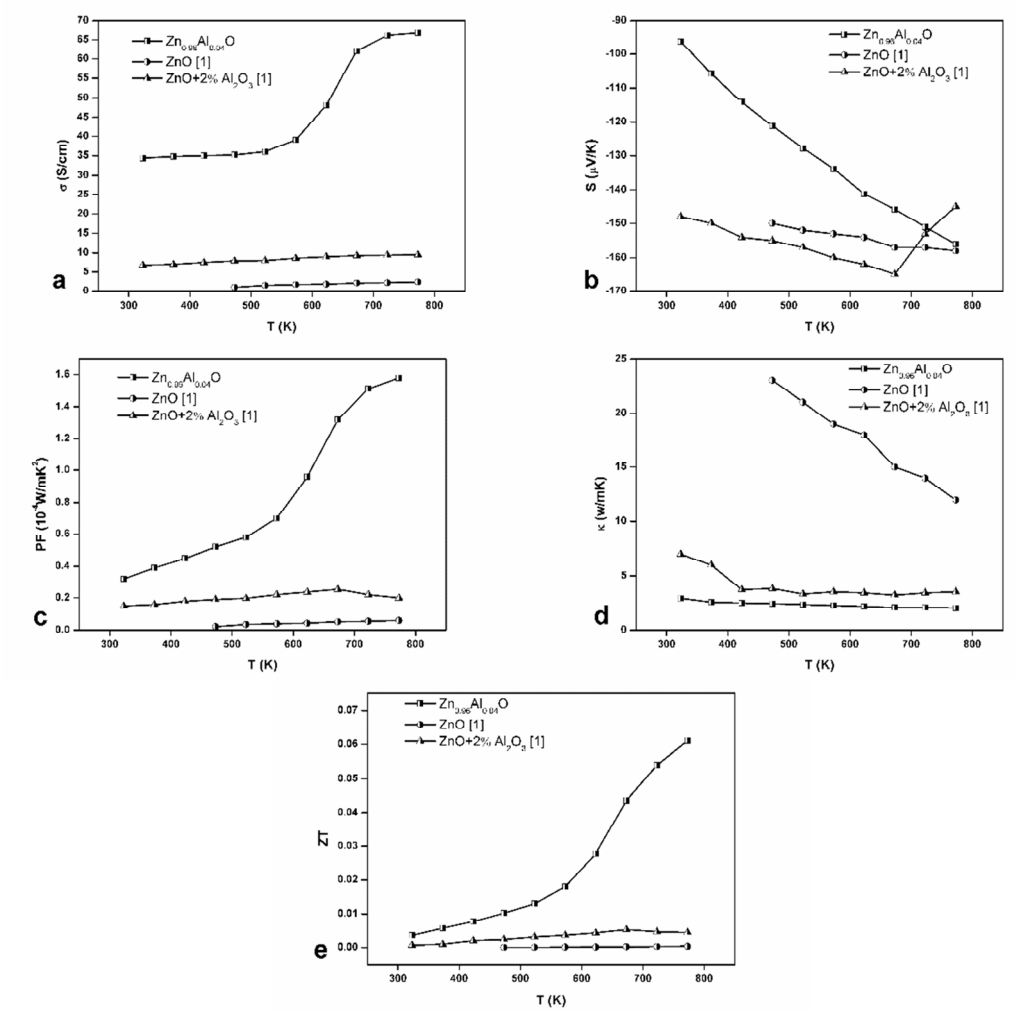


Fig. 3. Temperature dependence of the thermoelectric properties of $Zn_{0.96}Al_{0.04}O$ for (a) electrical conductivity, (b) Seebeck coefficient, (c) power factor, (d) thermal conductivity, (e) Dimensionless Fig. of Merit as comparing to results of previous works of the ZnO results.

Due to the sintered $Zn_{0.96}Al_{0.04}O$ sample displaying the high *ZT* value that that of the ZnO results, the $Zn_{0.96}Al_{0.04}O$ sample was used to fabricate thermoelectric module. The module was invented in the uni n-type module as shown in Fig. 4(a). The $Zn_{0.96}Al_{0.04}O$ thermoelectric module was fabricated in model of 1 and 2 legs

shape type of Uni n-type module. The testing power output of the $Zn_{0.96}Al_{0.04}O$ thermoelectric module was devalued in high temperature electric furnace as shown in Fig. 4(b). Fig. 4(b) shows diagram of arrangement for testing thermoelectric module. The testing was consisted of two thermocouples for measured temperature at hot side (T_h) and cold side (T_c) of the module. The heat source of this work was obtained from electrical furnace with temperature from room temperature to 1,200 °C. The electric voltage and current were measured by using multi-meter measurement. Fig. 4(c) shows the graph of temperature depended of output voltage (*Vol*) and electrical current (*I*) for one leg of the $Zn_{0.96}Al_{0.04}O$ thermoelectric module. The results displayed that the *Vol* and *I* values were increased with increasing different temperature as expected. The maximum values of the *Vol* and *I* were 105 mV and 0.95 mA at ΔT = 600 °C, respectively.

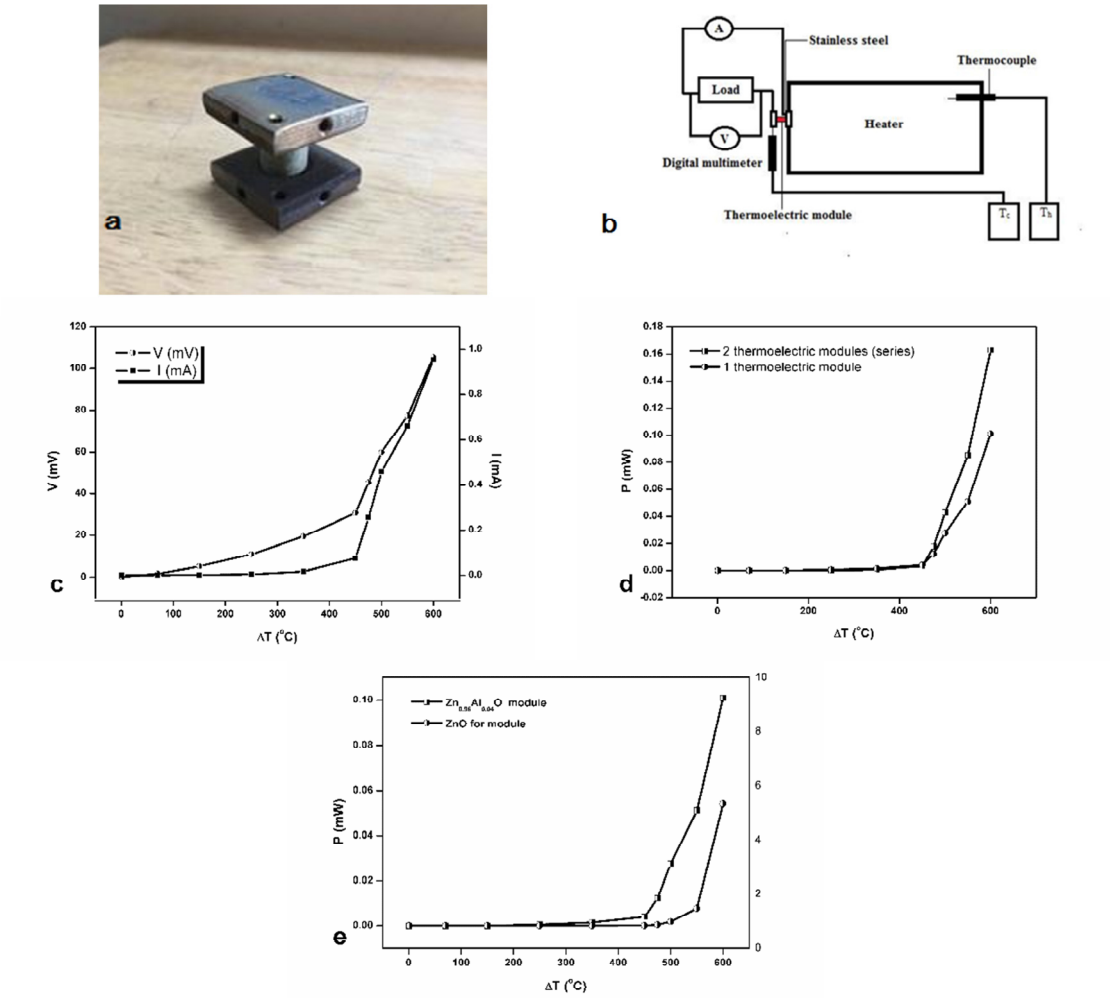


Fig. 4. (a) thermoelectric module (b) diagram of arrangement for testing thermoelectric module (c) Temperature dependence of the *Vol* and *I* value for $Zn_{0.96}Al_{0.04}O$ 1 module (d) Temperature dependence of output power for $Zn_{0.96}Al_{0.04}O$ one and two thermoelectric modules (e) comparison of output power value for $Zn_{0.96}Al_{0.04}O$ and ZnO modules.

Fig. 4(d) shows the measured output power of one leg and two legs of the $Zn_{0.96}Al_{0.04}O$ thermoelectric module. The results showed that the power for both modules was increased with increase different temperature. The power was 0.1 mW and 0.14 mW at 900 °C (at ΔT = 600 °C) for one leg and two legs of the $Zn_{0.96}Al_{0.04}O$ thermoelectric modules ,respectively. The results revealed that the power of the two legs of thermoelectric module were large than that of the one leg of thermoelectric module at the temperature higher that 450 °C. This implied that the $Zn_{0.96}Al_{0.04}O$ thermoelectric module can produce more output power when using many modules and higher different

temperature. Fig. 4(e) shows the comparison of output power value of the invented $Zn_{0.96}Al_{0.04}O$ thermoelectric module and the invented ZnO thermoelectric module in this work. The results show that the output power value of the invented $Zn_{0.96}Al_{0.04}O$ thermoelectric module was higher than that of the fabricated ZnO thermoelectric module.

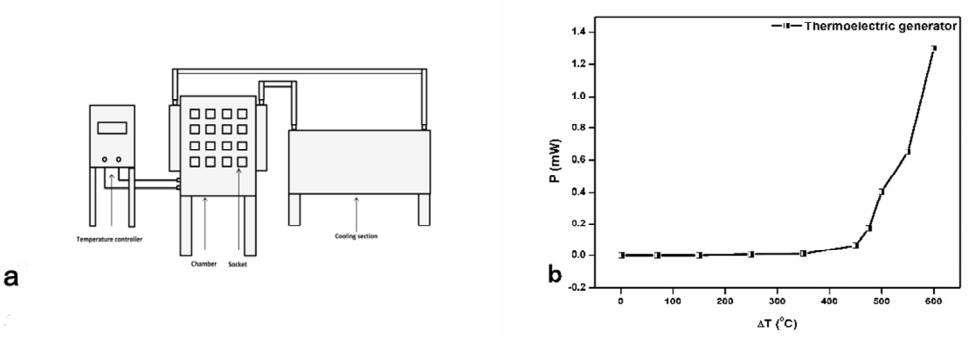


Fig. 5. (a) thermoelectric generator with the heat chamber and water cooler (b) output power versus temperature difference.

By above reason, the results pointed out that the $Zn_{0.96}Al_{0.04}O$ thermoelectric module displayed the high output power at high different temperature with using several thermoelectric modules. Also, this work applied the invented $Zn_{0.96}Al_{0.04}O$ thermoelectric module to fabricate thermoelectric generator. The $Zn_{0.96}Al_{0.04}O$ thermoelectric generator was machine which can convert temperature difference directly into electricity with attached $Zn_{0.96}Al_{0.04}O$ thermoelectric modules. Fig. 5(a) shows the schematic of the $Zn_{0.96}Al_{0.04}O$ thermoelectric generator. The $Zn_{0.96}Al_{0.04}O$ thermoelectric generator was consisted of heat chamber, heat source (liquid gas), temperature controller, cooling section and the $Zn_{0.96}Al_{0.04}O$ thermoelectric modules. The sixteen $Zn_{0.96}Al_{0.04}O$ legs thermoelectric modules were attached in socket at front side of the heat chamber. The heat chamber was heat source as generated from liquid gas. The heat chamber was used to generate high temperature up to 800 °C for supporting hot side (T_h) of the $Zn_{0.96}Al_{0.04}O$ thermoelectric modules. The cold side (T_c) of the $Zn_{0.96}Al_{0.04}O$ thermoelectric modules was controlled to low temperature by using water cooling from cooling section to keep the temperature difference of the modules. The electric voltage and current were measured by using digital multi-meter and then, the electric power was calculated. Fig. 5(b) shows the temperature difference dependence of output power of sixteen $Zn_{0.96}Al_{0.04}O$ legs of the thermoelectric generator. The results showed that the highest value of the output power for the sixteen $Zn_{0.96}Al_{0.04}O$ legs of the thermoelectric generator was 1.4 mW at 800 (at ΔT = 600 °C). Totally, the results implied that the tended of output power was increased with increasing temperature difference. Obviously, this work revealed that the $Zn_{0.96}Al_{0.04}O$ thermoelectric generator can be applied for electric conversion from heat at high temperature.

4. Conclusion

The ZnO and $Zn_{0.96}Al_{0.04}O$ samples were synthesized for thermoelectric materials and fabrication thermoelectric module. The sample was prepared by solid state reaction, and confirmed phase by using X-ray diffraction. The grain size of the ZnO was decreased with doping aluminum and this can influence significantly the thickness of the $ZnAl_2O_4$ layer at the grain boundaries during sintering. The thermoelectric performance of $Zn_{0.96}Al_{0.04}O$ material as σ, S, PF value displayed value higher than that of the ZnO based at the whole temperature and the highest value of ZT was contained 0.06 at 500 °C. The sintered $Zn_{0.96}Al_{0.04}O$ sample was improved thermoelectric properties as expect. The $Zn_{0.96}Al_{0.04}O$ thermoelectric module displays the output power as higher than that of the invented ZnO thermoelectric module. This work revealed that the $Zn_{0.96}Al_{0.04}O$ thermoelectric generator can be applied for electric conversion from heat at high temperature. The maximum output power of the sixteen $Zn_{0.96}Al_{0.04}O$ legs thermoelectric generator was 1.4 mW at 800 (ΔT = 600 °C) for this work. Totally, the $Zn_{0.96}Al_{0.04}O$ thermoelectric generator tended to increase with increasing temperature and using more thermoelectric modules to make series or parallel, so the $Zn_{0.96}Al_{0.04}O$ thermoelectric generator can be applied for electric conversion from heat at high temperature.

Acknowledgements

Chesta Ruttanapun would like to acknowledge the Thailand Research Fund (TRF) and King Mongkut's Institute of Technology Ladkrabang (KMITL) (Contract Number: TRG5880013) for financial support. Addition, the authors would like to acknowledge the Science Research Fund, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang (KMITL), Ministry of Education, Thailand for financial support.

References

[1] Mele P, Matsumoto K, Azuma T, Kamesawa K, Tanaka S, Kurosaki J and Miyazaki K, Development of $Al_2O_3/Ca_3Co_4O_9$ module for thermoelectric power generation, Materials Research Society, 1166 (2009) 3-11.
[2] Goldsmid H J, Bismuth Telluride and Its Alloys as Materials for Thermoelectric Generation Materials, 7 (2014) 2577-2592.
[3] Park K, Ko K Y, Seo W S, Cho W S, Kim J G and Kim J Y, High-temperature thermoelectric properties of polycrystalline Zn1-x-yAlxTiyO ceramics, European Ceramic Society 27 (2007) 813-817.
[4] Zhang L, Tosho T, Okinaka N and Akiyama T, Thermoelectric Properties of Solution Combustion Synthesized Al-Doped ZnO, Materials Transactions, 49 (2008) 2869-2874.
[5] Morkoc H and Ozgur U 2009 Fundamentals Materials and Device Technology Zinc Oxide Wiley-VCH
[6] Zak A K and Majid W H X-ray analysis of ZnO nanoparticles by Williams-hall and size-strain plot, Methods Solid State Sci, 13 (2011) 251-256.
[7] Tekeli S Influence of alumina addition on grain growth and room temperature mechanical properties of $8YSCZ/Al_2O_3$ composites, Composites Science and Technology, 65 (2005) 967-972.
[8] Bernik S, Daneu N and Recnik, A Inversion boundary induced grain growth in TiO_2 or Sb_2O_3 doped ZnO-based varistor ceramics European Ceramic Society, 24 (2004) 3703-3708.
[9] Janotti A and Walle C G V D Fundamentals of zinc oxide as a semiconductor, Rep. Prog. Phys 72 (2009)
[10] Han L, Nong N V, Hung L T, Holgate T, Pryds N, Ohtaki M and Linderoth S, The influence of α- and γ-Al_2O_3 phases on the thermoelectric propertiesof Al-doped ZnO, Alloys and Compounds, 555 (2013) 291-296.
[11] Cai K F, Müller E, Drašar C and Mrotzek A, Preparation and thermoelectric properties of Al-doped ZnO ceramics Materials Science and Engineering, 104 (2003) 45-48.
[12] Michitaka O, Kazuhiko A and Kiyoshi Y, High Thermoelectric Performance of Dually Doped ZnO, Ceramics Electronic Materials, 38 (2009)
[13] Xiurong Q, Wen W, Shuchen L and Dechang J, Thermoelectric properties and electronic structure of Al-doped ZnO, Solid State Communications, 151 (2011) 332-336.