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Fabrication and Performance Analysis of AZO and MCCO as Thin Film-Thermoelectric Generator Materials

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Abstract

The purpose of this research was to determine the performance of AZO and MCCO materials as constituents of the thin film-thermoelectric generator module. The method used for fabrication is DC Magnetron Sputtering. The electrode material used is Ag and the substrate used is SiO_2 glass. The arrangement of the thin film used for the fabrication of the thermoelectric module is P-N-P-N-P-N-P-N-P-N (5 couples of p-n junctions). Based on the test results, the thickness of the thin film type N is 74.72 nm and type P is 90.34 nm. At the highest test temperature (300°C), the AZO Seebeck coefficient value is -108 μV/K while the MCCO Seebeck coefficient value is 350 μV/K, and the AZO electrical resistivity value is 0.07 Ω.m, while the MCCO electrical resistivity value is 0.36 Ω.m. The highest temperature difference given in the test of the AZO and MCCO thin films thermoelectric module are 1.538℃ and the thermoelectric module can produce a voltage of 1,842 ± 0.047 mV, a Seebeck coefficient of 4 μV/K, and an efficiency of 0.44%. Based on this research, it can be concluded that the performance of AZO and MCCO thin film-thermoelectric modules will have better performance at temperatures around 300 – 350℃.

Keywords: *AZO; DC Magnetron Sputtering; MCCO; Thermoelectric Generator; Thin Film*

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INTRODUCTION

Energy consumption in this pandemic era (2020 – 2021) slightly decreased by around 7% from the previous year. However, it is estimated that energy consumption will increase again in early 2023 [1]. The increase in energy consumption will certainly be followed by an increase in CO_2 gas emissions which have an impact on global warming [2]. According to the Stated Policies Scenario (STEPS), it is estimated that CO_2 emissions in 2030 will reach 36 Gt. So that the government implements the Sustainable Development Scenario (SDS) with the hope that CO_2 gas emissions in 2030 will be below 27 Gt [1]. Thus, to support the achievement of SDS targets, it is necessary to develop renewable energy.

Renewable energy can be sourced from various things, such as sun, wind, biomass, geothermal, tidal, and so on [3]. Heat is one of the most abundant energy sources. Heat can be converted into electricity using a thermoelectric mechanism based on the Seebeck effect [4, 5]. Thermoelectric is a renewable energy that is quite easy to use, cheap to produce, and can be applied on a large or small scale [6]. Therefore, research on thermoelectric as renewable energy has a lot of potentials.

The performance of a thermoelectric material can be viewed from the Figure of Merit (Z) value such as Eq. (1).

$$ZT = \frac{S^2 \sigma T}{\kappa} \tag{1}$$

where T is the temperature (K), Z is the thermoelectric material's Figure of Merit, S is the Seebeck Coefficient (V/K), σ is the electrical conductivity (S/m), and κ is the thermal conductivity (W/K.m) [7]. Then, the magnitude of the Seebeck coefficient (S) can be written as Eq. (2) [8].

$$S = -\frac{\Delta V}{\Delta T} \approx \frac{1}{n} \tag{2}$$

Or

$$S = \frac{8\pi^2 {\kappa_b}^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^2 \tag{3}$$

Where n is the concentration of the carrier, m* is the effective mass of the carrier, e is the charge of the electron, kb is the Boltzman's constant, and h is the Planck's constant [9]. While the efficiency of a thermoelectric generator can be written as Eq. (4) [10]:

$$\eta = \frac{(T_h - T_c)(M-1)}{T_h\left(M + \frac{T_c}{T_h}\right)} \tag{4}$$

Where M is:

$$M = \frac{R_L}{R}\left(1 + Z\,\frac{T_h + T_c}{2}\right)^{\frac{1}{2}} \tag{5}$$

Where Th is the high temperature (K) while Tc is the low temperature (K).

So far, the commercially available thermoelectric modules have a stiff texture and are relatively large limiting their use in many ways. Then at this time began to be developed thermoelectric thin films [11] using various methods [12]. As written in Eq. (4), to obtain high efficiency from a thermoelectric module, a material that has a high Seebeck coefficient value, high electrical conductivity, and low electrical resistivity is needed. Thus, the choice of material has a major role in improving the performance of a thermoelectric module.

ZnO is an n-type material with good chemical and thermal stability at high temperatures, so it is suitable to be applied as a high-temperature thermoelectric [13 – 16]. Like ZnO, $CaCO_3$ is a p-type material with a high Seebeck coefficient and high electrical conductivity, making it suitable for a thermoelectric material [17]. Unfortunately, the resistivity of ZnO and $CaCO_3$ is still high enough to be used as a thermoelectric so doping of the material is needed [14 – 16]. As a group IIIa metal, aluminum has good conductivity so that it can reduce the resistive properties of ZnO [18] and withstand high temperatures [19]. And based on research conducted by [20], dopping Mn on p-type material will increase the electrical conductivity. It is hoped that with the two dopings given, a thermoelectric module with good performance will be obtained. Thus, it is important to know about the performance of AZO and MCCO as a constituent of thin-film thermoelectric generator modules with the hope of obtaining a low-cost thermoelectric material that can be applied at high temperatures.

METHODOLOGY

In this study, the doping material used as an n-type fulfills the following chemical equation:

$0.98ZnO + 0.01Al_2O_3 \rightarrow Zn0.98Al0.02O + 0.005O_2$

As for the p-type, the doping material used fulfills the following chemical equation:

$3CaCO_3 + \frac{7}{4}Co_2O_3 + \frac{1}{2}Mn + \frac{3}{8}O_2 \rightarrow Ca_3Co_{3.5}Mn_{0.5}O_9 + 3CO_2$

The electrode material used is Ag and the substrate used is SiO_2 glass. After doping the material, calcination is carried out in a furnace with a temperature of 800°C for 10 hours for type p while for type n it is carried out at a temperature of 500°C for 5 hours. After that, pressing was done with a pressure of 2500 Bar for 12 minutes so that the target solids were formed. Then sintering was carried out using a furnace at a temperature of 850°C for 12 hours for the p-type while for the n-type it was carried out at a temperature of 600°C for 5 hours.

After the target is formed, the sputtering process is carried out using a DC Magnetron Sputtering machine according to the conditions listed in Table 1.

Table 1. Sputtering Conditions.

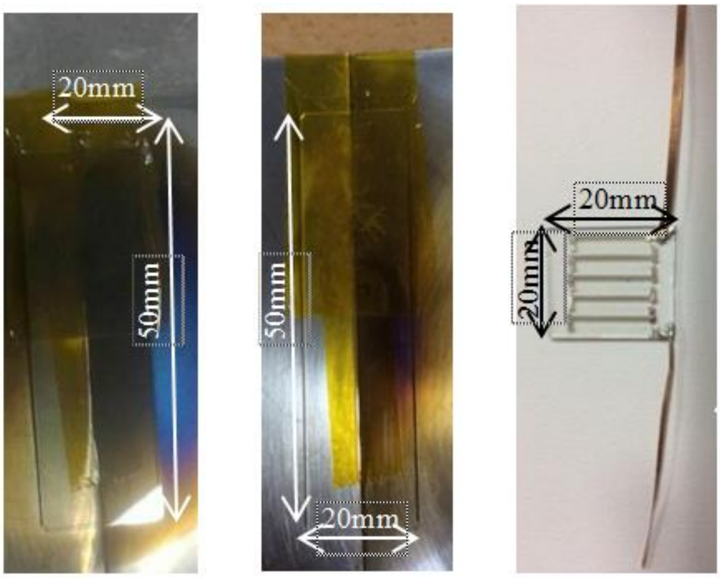
Parameter	P-Type	N-Type	Electrode
Base Pressure (Torr)	3.5×10^{-5}	3.5×10^{-5}	3.5×10^{-5}
Operation Pressure (Torr)	1.5×10^{-2}	1.3×10^{-2}	1.5×10^{-2}
Ar Flow Rate (sccm)	20	20	25
Voltage (Volt)	250	200	549
Current (mA)	100	100	150
Vacuum Chamber Temperature (°C)	18	20	18
Deposition Time (minute)	10	10	10

The sputtering process is carried out for p-type, n-type, then electrodes to form a thin film thermoelectric module.

After forming a thin film, several tests were carried out such as ZEM-3 to determine the electrical resistivity and Seebeck coefficients of AZO and MCCO thin-film thickness testing, output voltage (V_{out}) testing, Seebeck coefficient (S) testing, and efficiency (η) testing of AZO and MCCO thin film thermoelectric modules.

RESULTS AND DISCUSSION

The fabrication result of the thin film thermoelectric module can be seen in Fig. 1.



a b c

Figure 1. (a) p-type thin film, (b) n-type thin film, and (c) thin-film thermoelectric module

The connection of the two thin films of P and N types is P-N-P-N-P-N-P-N-P-N (5 couples p-n junction). After fabricating a thin film, the resistance test was carried out using a multimeter at room temperature (27°C) and the results showed that the resistance value for type P was 274.4 ± 4,722 Ω while for type N was 707.8 ± 10,569 Ω.

Furthermore, thin-film thickness testing was also carried out using the Tolansky Apparatus. The thickness of the thin-film measured for the N-type is 74.72 nm and for the P-type is 90.34 nm. The thickness of the film that is formed depends on the length of the sputtering process. The longer the sputtering process, the thicker the thin film that is formed because there will be many target atoms growing on the substrate.

Then, tests using the ZEM-3 were carried out to determine the electrical resistivity and Seebeck coefficient of the thin film. Electrical resistivity testing using ZEM-3 was carried out at temperatures of 100°C, 200°C, and 300°C. The test is carried out at a maximum temperature of 300^{O}C because the glass substrate used can crack at temperatures around 350^{O}C. As a generator thermoelectric module, a material should have a low resistivity value to conduct electricity well. And the results of the electrical resistivity test can be seen in Fig. 3.

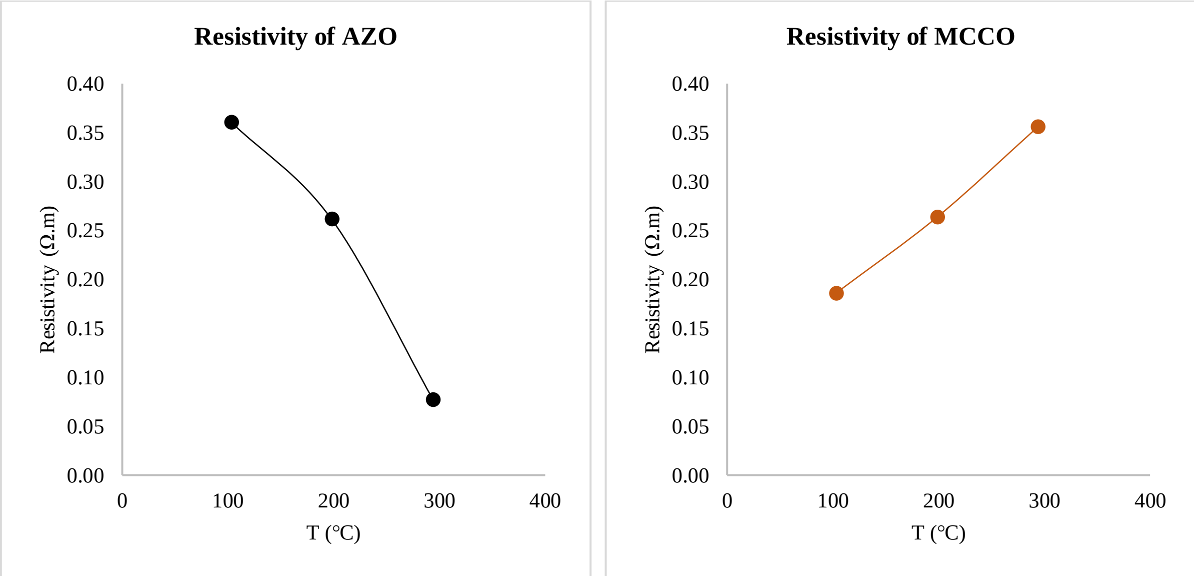


Figure 3. Resistivity test results

Based on the results of the tests that have been carried out, the electrical resistivity value of AZO decreases with increasing temperature, while the electrical resistivity value of MCCO increases with increasing temperature. AZO's electrical resistivity values are 0.36 Ω.m at 100^{O}C, 0.26 Ω.m at 200^{O}C, and 0.07 Ω.m at 300^{O}C. While the electrical resistivity value of MCCO is 0.18 Ω.m at 100^{O}C, 0.26 Ω.m at 200^{O}C, and 0.36 Ω.m at 300^{O}C. Based on research conducted by [21], pure ZnO has a very high resistivity, which is 10^{11} Ω.m at 100°C. Based on Fig. 3, it can be concluded that Al doping can reduce the resistivity of ZnO. While based on research conducted by [22], pure $CaCO_3$ has a resistivity value of 20 Ω.m at 100°C. Based on Fig. 3, it can be concluded that Mn doping can reduce the resistivity of $CaCO_3$. Thus, both materials are good for thermoelectric materials because they have a very low electrical resistivity value, which is less than 1 Ω.m up to a test temperature of 300^{O}C. Moreover, AZO material is good for application as a high-temperature thermoelectric material because the electrical resistivity value is inversely proportional to higher the temperature.

In addition, the Seebeck Coefficient (S) value of each type of thin-film was tested. Seebeck coefficient defines how sensitive a material is to produce stress when there is a temperature difference. So as a generator thermoelectric module, a material should have a high Seebeck coefficient value. The test results of the Seebeck coefficient can be seen in Fig. 4.

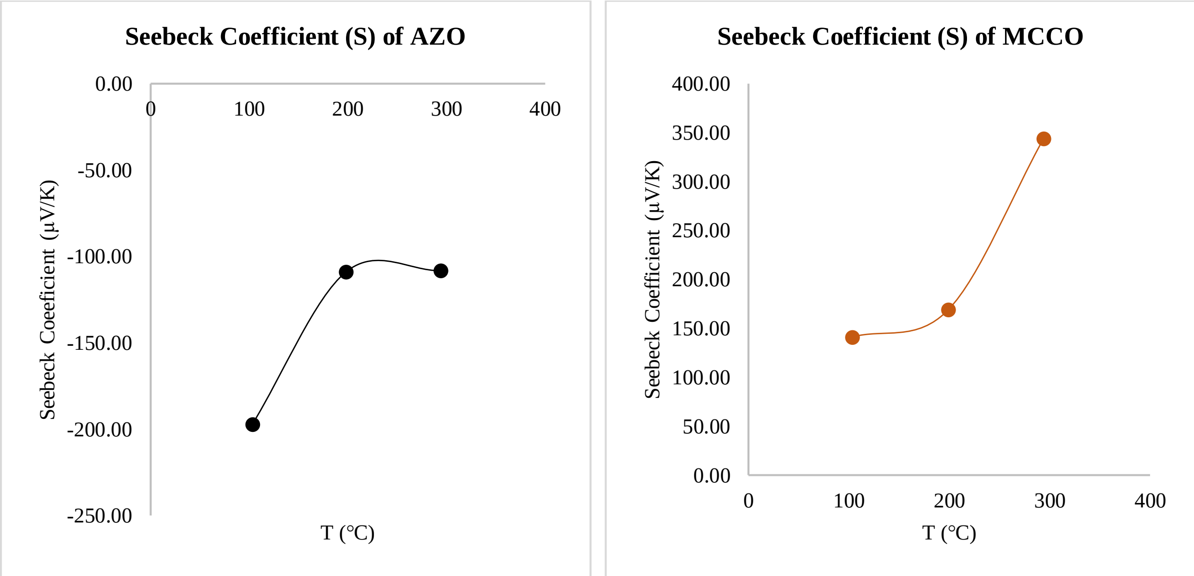


Figure 4. Seebeck coefficient test results

Based on the test, the Seebeck coefficient value of the two materials increases with increasing temperature. AZO's Seebeck coefficient value is -198 µV/K at 100^{o}C, -109 µV/K at 200^{o}C, and -108 µV/K at 300^{o}C. Meanwhile, the MCCO's Seebeck coefficient value is 140 µV/K at 100^{o}C, 170 µV/K at 200^{o}C, and 350 µV/K at 300^{o}C. Based on these data, AZO and MCCO materials are good to be applied as high-temperature thermoelectric constituent materials because the higher the temperature given to them, the higher the Seebeck coefficient value.

Then, testing the output voltage of the thermoelectric module is carried out with the results which can be seen in Fig. 5.

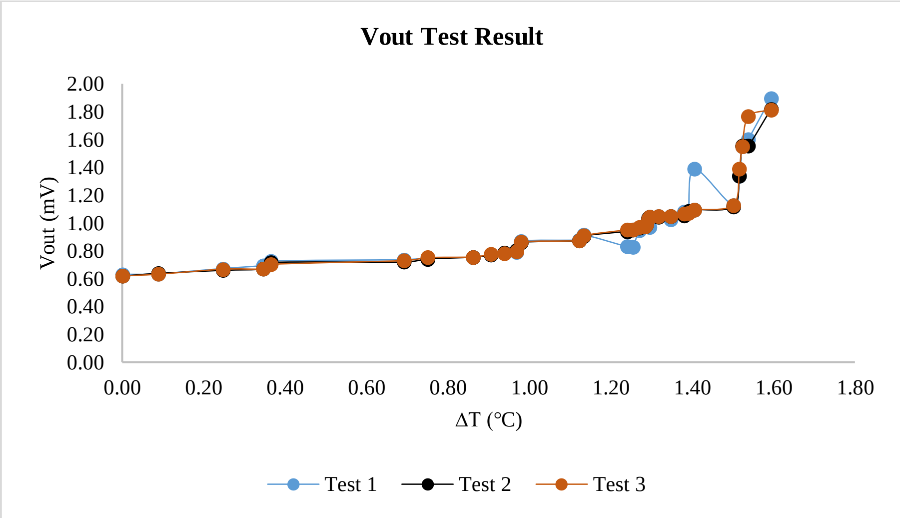


Figure 5. V_{out} test result

The test is carried out using an electrical power apparatus that can display data in real-time through the monitor screen. From the graph, it can be concluded that the greater the temperature difference that occurs, the greater the voltage generated. The voltage generated by the module has the order of millivolts. The largest temperature difference given in this test is 1,538°C and can produce a voltage of 1,842 ± 0.047 mV. This value is considered large because only a temperature difference of 1°C can produce a voltage of about 2 mV. The relationship between temperature rises and voltage is triggered by the Seebeck mechanism. From the test graph, it can be observed that at a temperature difference above 1°C, the increase in the graph is quite significant. This shows that the performance of this thin film thermoelectric module is getting better if the temperature difference is getting bigger. The performance of this thin film thermoelectric module improves considerably after a temperature difference of above 1°C.

After the V_{out} test is carried out, the Seebeck coefficient is calculated from the thermoelectric module that has been formed to prove the Seebeck mechanism, where there will be an increase in voltage along with an increase in temperature. The calculation is carried out using Eq. (2) and the results are obtained like the graph in Fig. 6.

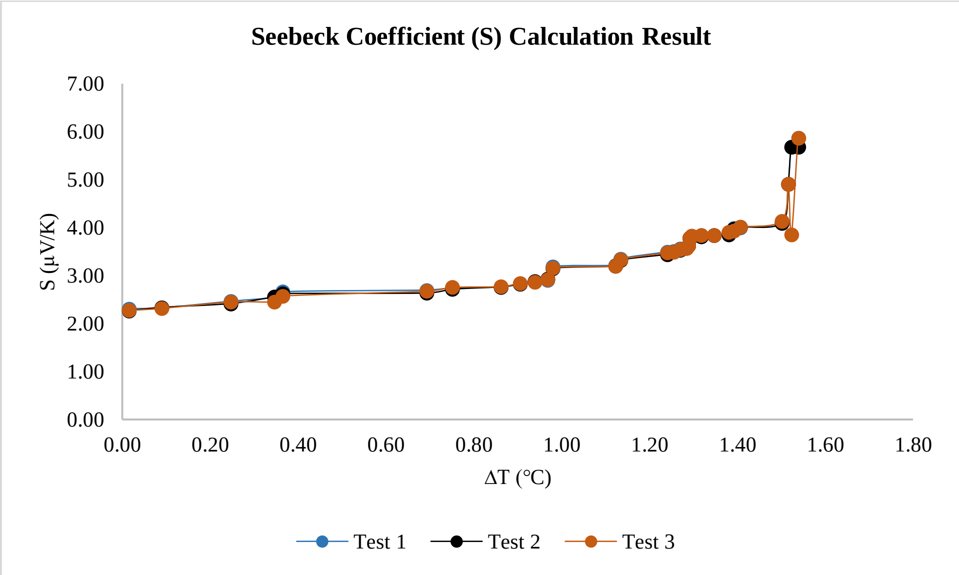


Figure 6. Seebeck coefficient (S) calculation of thin-film thermoelectric module

From the graph above, it can be observed that there is a significant increase in the value of the Seebeck coefficient when the temperature difference is more than 1°C. The Seebeck coefficient value of this thin-film thermoelectric module reaches 3 µV/K at a temperature difference of about 2°C. This value is a big value for the performance of a thin film thermoelectric module because most other thermoelectric materials such as AgSbTe, which is a thermoelectric elementary material, with a coefficient value of about 1.09 µV/K at a temperature difference of 1.45°C [23].

Then, for the thermoelectric generator application, it is important to know the efficiency of the thermoelectric module. Efficiency calculations are carried out using Eq. (5), where the external resistance (RL) given during the test is 50 kΩ. Based on the results of the calculation of the efficiency of the thermoelectric module, the results are as shown in the graph in Fig. 7.

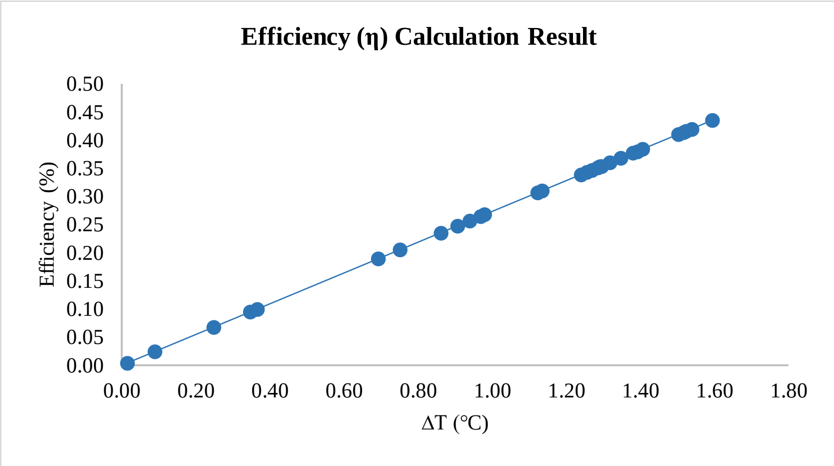


Figure 7. Efficiency (η) calculation of thin film-thermoelectric module

The results of the efficiency calculation show a linearly increasing graph. This means that the use of this thin film-thermoelectric module will be better if the temperature difference is greater. At the lowest temperature difference, namely 0.015°C, the efficiency of the thermoelectric module is 0.004%. Whereas at the highest temperature difference, namely 1.538°C, the efficiency of the thermoelectric module was 0.44%. If the temperature difference given is even higher, the efficiency produced by the thermoelectric module can still increase again.

CONCLUSIONS

This paper has reported the results of research on the use of AZO and MCCO as thermoelectric materials for thin films. Thermoelectric thin films are fabricated using the DC Magnetron Sputtering method and using Ag material as electrodes. Based on the test results, the thickness of the thin layer type N is 74.72 nm and type P is 90.34 nm. The value of the Seebeck AZO and MCCO coefficients increases with increasing test temperature. The electrical resistivity value of AZO decreases with increasing test temperature, while the electrical resistivity of MCCO increases with increasing test temperature. However, both materials can be said to have good performance when used as a thermoelectric module because the electrical resistivity value is less than 1 Ω.m until the test temperature is 300ºC. The largest temperature difference given in this test is 1.538°C and the thermoelectric module can produce a voltage of 1.842 ± 0.047 mV while the efficiency reaches 0.44%. The use of this thin-film thermoelectric is limited to a temperature of 350°C because the SiO2 glass substrate used can crack at this temperature. Thus, it can be concluded that the performance of AZO and MCCO thin-film thermoelectric modules will have better performance at temperatures around 300 – 350°C.

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