P-Ca$_3$Co$_4$O$_9$/n-Zn$_{0.98}$Al$_{0.02}$O module for high temperature thermoelectric generator

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Abstract. The thermoelectric generators can generate electrical power from different temperatures of the top and bottom side thermoelectric modules or devices using n- and p-types thermoelectric materials. We synthesized the p-type Ca$_3$Co$_4$O$_9$ and n-type Zn$_{0.98}$Al$_{0.02}$O thermoelectric materials by solid-state reaction (SSR) and hot-pressing (HP) methods then measured thermoelectric properties such as Seebeck coefficient, electrical resistivity, and thermal conductivity. The thermoelectric module of π-shape was fabricated 2 pair p-n junction then measured the electrical voltage, power, and efficiency. It was found that we obtained the single phase of Ca$_3$Co$_4$O$_9$ and Zn$_{0.98}$Al$_{0.02}$O thermoelectric materials. The thermopower of Ca$_3$Co$_4$O$_9$ and Zn$_{0.98}$Al$_{0.02}$O thermoelectric materials are measured by using steady-state method at hot side 976 K. The electricity of thermoelectric cells was increased with increasing temperature difference from 28–603 K. The thermoelectric cells p-n junction 2 pairs generated a maximum voltage about 93.04 mV, power 8 mW and efficiency of 0.23 % at temperature difference of 735 K (hot side 976 K). So, the thermoelectric module has been feasible to fabricate thermoelectric generators and developed a method for fabrication of high stability modules.

Keywords: Oxide thermoelectric generator, thermoelectric module π-shape, synthesis oxide thermoelectric materials, thermoelectric properties, thermoelectric device

1. Introduction
Nowadays, emerging global energy consumption drives the need for energy production, conservation, and management has intensified interest in the century due to the significant rate at which the world’s energy demand is growing because of population growth and industrialization [1] therefore means of power generation research studies on alternative energy resources [2]. A thermoelectric (TE) device is viable clean energy that can convert thermal energy into electrical energy when a temperature gradient is present at the Seebeck effect. While a reverse phenomenon called the Peltier effect enables the TE device to generate thermal energy from electrical energy [3]. TE energy conversion plays a significant role in power generation by recovering waste heat released from many heat sources [4]. Thermoelectric generators (TEGs) can convert thermal energy directly into electricity through the Seebeck effect when
a temperature difference is applied between their two sides [5]. However, TE devices have not been widely used for power generation because of their low conversion efficiencies [6] and TE modules and generators typically consist of p- and n-type TE legs connected electrically in parallel and series [7]. The efficiency of thermoelectric energy conversion is determined by the dimensionless figure of merit:

$$ZT = \frac{S^2 T}{\rho \kappa}$$

(1)

Where $S$ is Seebeck coefficient, $\rho$ is electrical resistivity, $\kappa$ is thermal conductivity, and $T$ is absolute temperature [8].

In order to increase $ZT$, it is necessary to decreasing $\rho$ and increasing $S$ and reducing $\kappa$ at the same time.

The thermoelectric device has two functions are thermoelectric generator and thermoelectric cooling, on the other hand, thermoelectric creating a cool side and a hot side by using an electric current, that is Peltier or cooling [9]. In addition, the thermoelectric materials have a three-temperature range, consisted of low-temperature range, medium temperature range, and high-temperature range [10]. In the low-temperature range materials, the most popular is bismuth telluride and antimony telluride [11]. In the medium temperature range, the silicide materials such as magnesium silicide and manganese silicide to use in this range. In the last of high-temperature range is an oxide material such as NaCo$_2$O$_4$ [12–13] Ca$_3$Co$_4$O$_9$ [14–15], Zn$_3$In$_2$O$_8$ [16], SrTiO$_3$ [17–18], CaMnO$_3$ [19–20], and ZnO [21–25]. The over the years the performance of the oxide material has been enhanced by the addition of several depots, the improvement of the grain connection, and a variety of methodologies. However, the figure of merit of thermo-electric oxides is lower than 1 ZT about 0.1–0.8 at $T = 800$–1300 K [9, 26]. Among these oxide TE, Ca$_3$Co$_4$O$_9$ [27] and ZnO [28] have been considered as p- and n-type oxides, respectively, due to their relatively high ZT values at high temperatures.

Our work focuses on the generator function and high-temperature range from the oxide material, resist oxidation reaction, and feasibility of using for a long time. We choose p-type Ca$_3$Co$_4$O$_9$/n-Zn$_{0.98}$Al$_{0.02}$O for the fabrication of the thermoelectric cells because p-type Ca$_3$Co$_4$O$_9$ showed low electrical resistivity and low thermal conductivity and slightly low Seebeck coefficient and n-type Zn$_{0.98}$Al$_{0.02}$O are shown high Seebeck coefficient, low thermal conductivity but high electrical resistivity, for this reason, we need to be matching for fabrication TE cell.

2. Materials and Methodology

2.1 Synthesis

Powders of p-type Ca$_3$Co$_4$O$_9$ and n-type Zn$_{0.98}$Al$_{0.02}$O were prepared by conventional solid-state synthesis starting from the oxides and press to pellet by hot pressing (HP) method. For n-type we chose Zn$_{0.98}$Al$_{0.02}$O as we found this concentration optimal for the thermoelectric properties. The next step was the sintering of the powders by HP to produce pellets for thermoelectric characterization and the production of cells.

2.1.1 Material Preparation and of p-type

Powders of p-type Ca$_3$Co$_4$O$_9$ were prepared from calcium carbonate powder CaCO$_3$ (99%, QRëCTM.) and cobalt oxide powder Co$_3$O$_4$ (99.5%, Aldrich) then their powders were weighed in proper stoichiometric amounts. The precursor powder was mixed by a planetary ball mill (planetary ball mill PM400 RETSCH) was employed to mix Ca$_3$Co$_4$O$_9$ powder in agate grinding jar sizes 500 ml with by 5 mm diameter agate balls with the ball-per-powder 18 balls for 10 g at 350 rpm for 5 h, then Ca$_3$Co$_4$O$_9$ powder was calcined at 1073 K for 10 h in air. The calcined powder was pressed for pellets by a uniaxial HP at 1123 K with heating rate of 4 °C/min and under pressed 60 MPa for 1 h in Ar atmosphere after that Ca$_3$Co$_4$O$_9$ bulk sample was annealed at 1023 K in air.
2.1.2 Material Preparation of n-type Powders of n-type Zn$_{0.98}$Al$_{0.02}$O were prepared from ZnO (99.5%, QRëC™.) and Al$_2$O$_3$ (95%, Ajax Finechem Pty Ltd.) then their powders were weighed in proper stoichiometric amounts, and then mixed by the planetary ball mill using agate balls and vial in ethanol for 24 h at 350 rpm and dried at 353 K for 24 h. The mixed powder was calcined at 773 K for 5 h in air. The calcined powder was pressed for pellets by HP method (OTF-1200x-VHP-4). Which the HP has cylindrical graphite die with 20 mm inner-diameters and under pressed 60 MPa at 1173 K with heating rate 4 ºC/min for 1 h in Ar atmosphere. The pellets were annealed by furnace at 1423 K for 5 h in the air.

The bulk Ca$_3$Co$_4$O$_9$ and Zn$_{0.98}$Al$_{0.02}$O was cut to size $3 \times 3 \times 15$ mm$^3$ for measurement of the Seebeck coefficient and electrical resistivity by ZEM-3(M10) was gauged in the temperature ranging from room temperature to 1023 K. The thermal conductivity was calculated from thermal diffusivity measured by the laser flash method using a Netzsch LFA-457 apparatus, with a sample size of diameter 9.5 mm and thickness 1 mm can be calculated from the equation:

$$\kappa = \alpha d C_p$$  \hspace{1cm} (2)

where  $\kappa$ is Thermal conductivity  
$C_p$ is heat capacity  
$\alpha$ is thermal diffusivity  
$d$ is density

Heat capacity was calculated from the equation of Dulong-Petit:

$$C_p = 3nR$$  \hspace{1cm} (3)

where  $n$ is the number of atoms per formula unit  
$R$ is the gas constant.

2.2 Fabrication thermoelectric cells Thermoelectric cells were designed by solid works program and assembly by silver plate. The design of thermoelectric cells was stated from assigning the substate size of $25 \times 25 \times 1$ mm$^3$ for 2 pair. Thermoelectric materials were used in size of $3.5 \times 3.5 \times \text{6 mm}^3$ and as shown in Figure 1. The materials were cut into $3.5 \times 3.5 \times \text{6 mm}^3$ rectangular legs; p-type Ca$_3$Co$_4$O$_9$ and n-type Zn$_{0.98}$Al$_{0.02}$O then the materials were painted with silver paste on top and bottom, then annealed of 1073 K for 30 minutes in air heating and cooling used 5 K/min. The two-couple annealed p and n legs have been attached to an alumina substrate size of $25 \times 25 \times \text{1 mm}^3$, which etched two columns by using a silver paste, then the silver plate attached on top for joint p and n legs to $\pi$-shape. The $\pi$-shape TE cell was drying on hot plate 10 minutes for dried silver paste, then the TE cell metalized of 1073 K 30 minutes in air heating and cooling used 5 K/min. When the cell cooled at room temperature connected red and black wire for positive in p and negative in n legs, respectively, then test the power and the failure temperature limit temperature used for TE cell and module.

![Figure 1.](image)

**Figure 1.** shows (a) cells design of thermoelectric device configuration and (b) $\pi$-shape thermoelectric cells.
2.3 Power generation measurement of Thermoelectric generator

The power generation of Thermoelectric generator described above was installed a water cooling and was under a heater, placed over the cells. To measure the temperatures of hot and cold side temperatures, the two K-type thermocouples were attached on the thin mica plate of high temperature and low-temperature sides using an alumina substrate, respectively. A photograph of the output power measurement of thermoelectric module is shown in Figure 2. The output power (W) was calculated by the output voltage (V) and current (I) caused by changing a resistor.

![Figure 2](image)

**Figure 2.** Show (a) the schematic diagram of the power generation measurement of thermoelectric generator, (b) Performance measurement of thermoelectric generator.

3. Results and Discussion

X-ray diffraction pattern analysis by X-ray diffraction technique from 10° to 80° step 0.02° in 1 s, and 2θ angle with CuKα-1 (l = 1.541 Å) at 40 kV and 30 mA, radiation utilizing a Shimadzu diffractometer, XRD-6100 at room temperature from Ca$_3$Co$_4$O$_9$ powder, hot pressing the diffraction peaks, indexed, by comparison, was PDF# 00-058-0661, as shown in Figure 3 were accomplished for space group 8 Cm (C 1 m 1). The main diffraction peaks indicate that the composites are composed of Ca$_3$Co$_4$O$_9$ phases [29]. A little impurity phase can also be observed in the composites has shown a single phase with the Monoclinic structure. These observed peak positions are different from the calcined sample pack. The intensity of (002) peaks are initiated peaks for detected to the other (hkl) peaks conditions, the (002), (003), (004), (113), (020), (005), (202), (203) and (006) planes on the base of Ca$_3$Co$_4$O$_9$ indicated a strong preference of all samples.

![Figure 3](image)

**Figure 3.** Indexed XRD patterns of Ca$_3$Co$_4$O$_9$ from the hot pressing at 1123 K for 1 h in Ar atmosphere.
The XRD patterns analysis by X-ray diffraction technique from 30° to 80° step 0.02° in 1 s, and 20 angle with CuKα-1 (λ = 1.541 Å) at 40 kV and 30 mA, radiation utilizing a Shimadzu diffractometer, XRD-6100 at room temperature of Zn$_{0.98}$Al$_{0.02}$O are shown in Figure 4. Which all peaks were corresponded with the crystal structure of ZnO ICDD PDF #00-036-1451 and indicated a hexagonal wurzite structure space group of P6$_3$mc (186) [30]. These observed peak positions are different from the calcined sample pack. The intensity of (101) peaks are initiated peaks for detected to the other (hkl) peaks conditions, the (100), (002), (002), (110), (103), (200), (112), (201), (204) and (202) planes on the base of Zn$_{0.98}$Al$_{0.02}$O indicated a strong preference of all samples. The obtained phase is pure and no peak was observed to correspond to aluminium, which may indicate that aluminium atoms were successfully incorporated in the ZnO lattice.

![Figure 4](image)

Figure 4. Indexed XRD patterns of Zn$_{0.98}$Al$_{0.02}$O from the hot pressing at 1173 K for 1 h in Ar atmosphere.

The crystallite size was calculated by the Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos(\theta)}$$  \hspace{1cm} (4)

where $D$ is the mean particles size, $K$ is a Scherrer constant = 0.9, $\lambda = 1.5406$ Å is the wavelength of the used radiation CuKα1, $\beta$ is the FWHM and $\theta$ is the Bragg diffraction angle [31]. The lattice parameters, $c/a$ lattice ratio, density and relative density of Ca$_3$Co$_4$O$_9$ and Zn$_{0.98}$Al$_{0.02}$O [32] are shown in Table 1. The lattice parameters of Ca$_3$Co$_4$O$_9$ $(a, b, c)$ and volume unit cell $(V)$ was calculated according to the following equation (5) and (6), respectively.

$$\frac{1}{d^2} = \frac{1}{\sin^2\beta}\left(\frac{h^2}{a^2} + \frac{k^2 \sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos\beta}{ac}\right)$$  \hspace{1cm} (5)

$$V = abc \sin\beta$$  \hspace{1cm} (6)

The lattice parameters of Zn$_{0.98}$Al$_{0.02}$O $(a, c)$ and volume unit cell $(V)$ was calculated according to the following equation (7) and (8), respectively.

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}$$  \hspace{1cm} (7)

$$V = \frac{\sqrt{3}a^2c}{2}$$  \hspace{1cm} (8)
Table 1. Show crystallite size, lattice parameter, \( c/a \) lattice ratio, density and relative density of \( \text{Ca}_3\text{Co}_4\text{O}_9 \) and \( \text{Zn}_{0.98}\text{Al}_{0.02}\text{O} \).

| Materials       | Crystallite Size (nm) | Lattice Parameter (Å) | \( c/a \) lattice ratio | unit cell volume (Å\(^3\)) | Density (g/cm\(^3\)) | Relative density % |
|-----------------|-----------------------|-----------------------|--------------------------|-----------------------------|----------------------|-------------------|
| \( \text{Ca}_3\text{Co}_4\text{O}_9 \) | 45.832                | 4.8734                | 4.4722                   | 10.853                      | 2.2270               | 211.460           | 4.72               |
| \( \text{Zn}_{0.98}\text{Al}_{0.02}\text{O} \) | 51.851                | 3.2490                | 3.2490                   | 5.2064                      | 1.6024               | 47.595            | 94.50              |

The morphology of the \( \text{Ca}_3\text{Co}_4\text{O}_9 \) and \( \text{Zn}_{0.98}\text{Al}_{0.02}\text{O} \) powders is shown in Figure 5. After HP-sintering, the grain size of \( \text{Ca}_3\text{Co}_4\text{O}_9 \) is observed that grain does grow larger after sintering and exhibited a dense microstructure of lamellar grains in size and strength. \( \text{Zn}_{0.98}\text{Al}_{0.02}\text{O} \) presented randomly oriented grains and increasing aluminum content the morphological to Spherical shape with a homogeneous distribution of the particles which correspond to the report [33].

![Figure 5](image.png)

**Figure 5.** SEM images at magnifications 5000 of (a) \( \text{Ca}_3\text{Co}_4\text{O}_9 \) and (b) \( \text{Zn}_{0.98}\text{Al}_{0.02}\text{O} \).

The Seebeck coefficient (S) and electrical resistivity (\( \rho \)) of \( \text{Ca}_3\text{Co}_4\text{O}_9 \) and \( \text{Zn}_{0.98}\text{Al}_{0.02}\text{O} \) were measured by a ZEM-3 technique at room temperature to 1073 K. Figure 6 shows the dependence of the Seebeck coefficient of \( \text{Ca}_3\text{Co}_4\text{O}_9 \) and \( \text{Zn}_{0.98}\text{Al}_{0.02}\text{O} \), which \( \text{Ca}_3\text{Co}_4\text{O}_9 \) shows positive-type and maximum value about 186 (\( \mu \text{V/K} \)) at 973 K and \( \text{Zn}_{0.98}\text{Al}_{0.02}\text{O} \) shown negative-type maximum about \( -408 \) (\( \mu \text{V/K} \)) at 1073 K together with references. It’s what found that the Seebeck coefficient of our work at high temperature has a high value compared with references.
Figure 6. The dependence of the Seebeck coefficient on the temperature of Ca$_3$Co$_4$O$_9$ and Zn$_{0.98}$Al$_{0.02}$O together with references.

The temperature dependence of the electrical resistivity Ca$_3$Co$_4$O$_9$ and Zn$_{0.98}$Al$_{0.02}$O shows in figure 7. Ca$_3$Co$_4$O$_9$ was similar behavior corresponding with metal to semiconducting transition in the range of 273–1073 K. Zn$_{0.98}$Al$_{0.02}$O showed a semiconducting behavior over the whole measured temperature range at room temperature to 1073 K and electrical resistivity value decreased with increasing of temperature content while Ca$_3$Co$_4$O$_9$ value increased with increasing temperature content. The dependence of the thermal conductivity on the temperature of Ca$_3$Co$_4$O$_9$ and Zn$_{0.98}$Al$_{0.02}$O shows in figure 8 found that the thermal conductivity of the results of all samples was decreased with increasing temperature. At temperature 1073 K Ca$_3$Co$_4$O$_9$ thermal conductivity value decreased to 1.38 (W/m K) and the Zn$_{0.98}$Al$_{0.02}$O thermal conductivity value decreased to 1.79 (W/m K) same temperature.

Figure 7. The dependence of the electrical resistivity on the temperature of Ca$_3$Co$_4$O$_9$ and Zn$_{0.98}$Al$_{0.02}$O together with references.
Figure 8. The dependence of the thermal conductivity on the temperature of Ca$_3$Co$_4$O$_9$ and Zn$_{0.98}$Al$_{0.02}$O together with references.

The dependence of the Dimensionless figure of merit on the temperature of Ca$_3$Co$_4$O$_9$ and Zn$_{0.98}$Al$_{0.02}$O shows in figure 9. The maximum ZT values of Ca$_3$Co$_4$O$_9$ and Zn$_{0.98}$Al$_{0.02}$O shown 0.0915 and 0.2882 at 1073 K. Plots of thermoelectric properties vs. temperature are reported while values at temperature 1073 K are summarized in Table 2.

Figure 9. The dependence of the Dimensionless figure of merit on the temperature of Ca$_3$Co$_4$O$_9$ and Zn$_{0.98}$Al$_{0.02}$O together with references.
Table 2. Summary of the thermoelectric properties of Ca$_3$Co$_4$O$_9$ and Zn$_{0.98}$Al$_{0.02}$O at 1073 K

| Materials     | Temperature HP (K) | Thermoelectric properties |
|---------------|-------------------|---------------------------|
|               |                   | S (µV/K)                  | ρ (mΩ cm) | κ (W/m K) | ZT  |
| Ca$_3$Co$_4$O$_9$ | 1123              | 186                       | 15.9      | 1.38      | 0.0915 |
| Zn$_{0.98}$Al$_{0.02}$O | 1173              | -408                      | 51.1964   | 1.79      | 0.2882 |

Figure 10 shown the open-circuit voltage was an output voltage and current distribution of TEG with thermoelectric cells assembled in series, the open-circuit voltage of the thermoelectric module was increased with increasing temperature difference from 28–603 K. The 2 pairs p-n junction thermoelectric module generated maximum open-circuit voltage 87.92 (mV) at a temperature different 345 K at hot side temperature 976 K in a 30-time circle. Figure 11 shows the electric power shown at about 7.96 (mW) at a temperature different 345 K at hot side temperature 976 K in a 30-time circle. The module can be used at high temperature and stable with used in heat source 1473 K.

![Figure 10](image-url)

Figure 10. The dependence of the open circuit voltage on the temperature difference of TE cells 2 pairs.
Figure 11. The dependence of the electric power on the temperature difference of TE cells.

Figure 12. The dependence of the electric current on the temperature difference of TE cells.

Figure 12 show the electric current on the temperature difference of TE cells 2 pairs can be was calculated according to the following equation:

\[ I = \frac{P}{V} \]  \hspace{1cm} (9)

where \( I \) is electric current (A), \( P \) is electric power (W) and \( V \) is voltage (V)

which data of \( P \) and \( V \) from Figure 10 and 11 the maximum value of the electric current is 93.9 mA at temperature difference 489 K.
4. Conclusion
Successfully for synthesis Ca$_3$Co$_4$O$_9$, and Zn$_{0.98}$Al$_{0.02}$O by solid-state reaction method and pelleted by the hot-pressing method be used to fabrication thermoelectric cells. The open-circuit voltage of thermoelectric cells was increased with increasing temperature difference from 28–603 K. The 2 pairs p-n junction thermoelectric cells generated maximum open-circuit voltage 87.92 (mV), and the eclectic power is shown about 7.96 (mW) at hot side temperature 976 K in a 30-time circle. The cells can be used at high temperature and stable with used in heat source 1473 K. The thermoelectric cells p-n junction 2 pairs generated maximum voltage about 93.04 mV, power 8 mW and efficiency of 0.229% at temperature difference 735 K (hot size 976 K) The cells have been feasibilities to fabrication thermoelectric generator. The module has been feasible to fabricate thermoelectric generators and developed a method for fabricated high stability module. In future work, we will improvement of the thermoelectric properties of the materials and thermoelectric modules for the high performance of the module.

Acknowledgments
This work has been funded by Project researchers and research to industry (RRi) PHD59I0003 and the Research Career Development (Grant No. RSA6180070). The ZME-3, XRD, Hotpress, and synthesis equipment were supported Center of Excellence on Alternative Energy and the Netzsch LFA-457 apparatus Institute for Integrated Radiation and Nuclear Science, Kyoto University, Osaka, Japan.

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