Uni-leg and π-shape thermoelectric cells

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Abstract

The thermoelectric generator (TEG) is a promising device for changing wasted heat energy into electricity, however the device is currently inefficient at generating power in this way. Exploration and development of the device’s efficiency is necessary for cell fabrication. In this work, comparisons are made between the power generation of uni-leg p-Ca$_3$Co$_4$O$_9$, uni-leg n-Ca$_{0.97}$Bi$_{0.03}$MnO$_3$ and p-n junction (π-shape) of p-Ca$_3$Co$_4$O$_9$, n-Ca$_{0.97}$Bi$_{0.03}$MnO$_3$. The dimensions of the thermoelectric material were a cross-sectioned area of 78.5 mm$^2$ with a height of 10 mm. The size of the alumina substrate was 25×25 mm$^2$. Thermoelectric cell fabrication used copper wire, series connected thermoelectric materials for the uni-legs cell and thin copper plate for the π-shape thermoelectric cell. The voltage, current, power output and conversion efficiencies were measured by the steady stat method. It was found that, in the 3 samples, uni-leg n-Ca$_{0.97}$Bi$_{0.03}$MnO$_3$ had the highest maximum voltage of 76.8 mV, with electrical current around 70 mA, electrical power of 5 mW and a conversion efficiency of 0.187% at a temperature difference of 200 K, which makes this fabricated thermoelectric device feasible.

Keywords: Uni-leg, Thermoelectric generator, π-shape, feasibility, p-n junction

1. Introduction

Nowadays, major energy consumption from fossil-fuels wastes a lot of heat through the use of such machines as engines and boiling systems. This wasted heat energy can be recovered and converted to electricity by thermoelectric devices that are small and have no moving parts. They also have low maintenance costs. Thermoelectric materials are materials that can generate electric power from heat and create temperature
differences from electricity. Thermoelectric devices consist of n and p types and use a Bi-Te system for commercial fabrication. However, thermoelectric material using a Bi-Te system is active in low temperatures of around 400-420 K [1-3]. Improved thermoelectric materials for medium and high temperatures use oxide material for fabricating thermoelectric devices, because of its stability and non-oxidation properties. However, the oxide thermoelectric material has low performance. The performance of materials is indicated by the dimensionless figure of merit; 

\[ ZT = S^2\sigma T / \kappa \]

where \( S \), \( \sigma \), \( T \) and \( \kappa \) are Seebeck coefficient, electrical conductivity, thermal conductivity and absolute temperature, respectively. Normally, thermoelectric devices consist of n and p types, but there is also fabrication of uni-legs which use thermoelectric material of a single type only, for fabricated thermoelectric devices. The reduction of a precursor for fabrication of the device will save costs and reduce the time needed for synthesis of the material. In this research project, the feasibility of fabricating a uni-leg thermoelectric device was studied by comparing the power generation of 3 samples. These samples were a p-type (uni-leg) \( \text{Ca}_3\text{Co}_4\text{O}_9 \), n-type (uni-leg) \( \text{Ca}_{0.07}\text{Bi}_{0.03}\text{MnO}_3 \) and p-n junction (π-shape) \( \text{p-Ca}_3\text{Co}_4\text{O}_9, \text{n-Ca}_{0.07}\text{Bi}_{0.03}\text{MnO}_3 \) [4]. The thermoelectric materials were synthesized by the solid state reaction method.

2. Materials and Methods

The p-\( \text{Ca}_3\text{Co}_4\text{O}_9 \) and n-\( \text{Ca}_{0.07}\text{Bi}_{0.03}\text{MnO}_3 \) bulks were prepared from powder p-\( \text{Ca}_3\text{Co}_4\text{O}_9 \) and n-\( \text{Ca}_{0.07}\text{Bi}_{0.03}\text{MnO}_3 \) using the solid state reaction method or SSR method. Firstly, calcium carbonate powder (\( \text{CaCO}_3 \) 100.09 g/mol, purity 99%, Sigma-Aldrich Co.) was mixed with cobalt oxide powder (\( \text{Co}_2\text{O}_3 \) 165.86 g/mol, purity 99.9%, Sigma-Aldrich Co.) for p-type. Then calcium carbonate powder was mixed with manganese dioxide (\( \text{MnO}_2 \) 86.94 g/mol, purity 99.9%, Ajax Finechem Pty Ltd.) and bismuth oxide (\( \text{Bi}_2\text{O}_3 \) 465.96 g/mol, purity 99.9%, Sigma-Aldrich Co) purity in molar ratios for n-type. The \( \text{CaCO}_3 \) and \( \text{Co}_2\text{O}_3 \) were mixed for p-\( \text{Ca}_3\text{Co}_4\text{O}_9 \) and \( \text{CaCO}_3 \), MnO2 and \( \text{Bi}_2\text{O}_3 \) were mixed for n-\( \text{Ca}_{0.07}\text{Bi}_{0.03}\text{MnO}_3 \) by wet ball milling, using DI water and \( \text{ZrO}_2 \) calcined at 1123 K 10 h and 1323 K 24 h in air, respectively. The calcined p-type powder was pressured at 21.57 MPa due to sintered bulks at 1223 K 12 h. The calcined n-type powder was pressured at 9.80 MPa for bulks sintered at 1423 K 36 h in air, respectively. Subsequently, the sintered bulks were cut and polished by using the precision saw and grinder polisher (Isomet Low Speed Saw and WetaServ 3000 Ltd, USA) to obtain the legs shape of the thermoelectric cell. The size of thermoelectric materials had a cross-section area of 78.5 mm\(^2\) and height of 10 mm. The thermoelectric cell was constructed by connecting it in series with thin copper wire electrodes, using silver paint and solder, connected on top and bottom to an alumina substrate. The efficiency of the cell was measured on its hot side at 673 K. The substrate used alumina plate with a size of 25x25 mm\(^2\).

3. Results and Discussion

The x-ray diffraction patterns of sintered powder p-type and n-type are presented in Fig. 1 and 2. The patterns of p-\( \text{Ca}_3\text{Co}_4\text{O}_9 \) and n-\( \text{Ca}_{0.07}\text{Bi}_{0.03}\text{MnO}_3 \) conformed to a single phase compound in Monoclinic and Orthorhombic structure and showed agreement to PDF# 00-058-0661 and PDF# 00-050-1746, respectively.
Fig. 3 shows the fabrication of a thermoelectric cell (a) uni-leg and (b) p-n type (π-shape). Fig. 4 and 5 show the temperature dependence of the Seebeck coefficient of the p-type and n-type increased with increasing temperature and trends more active than in high temperatures.

Fig. 1 XRD pattern of p-Ca₃Co₄O₉ powder sintered 1223 K 12 h

Fig. 2 XRD pattern of n-Ca₀.₉₇Bi₀.₀₃MnO₃ powder sintered 1423 K 36 h

Fig. 3 Fabrication Thermoelectric cell (a) uni-leg and (b) p-n type (π-shape)

Fig. 4 Temperature dependence of Seebeck coefficient p-Ca₃Co₄O₉

Fig. 5 Temperature dependence of Seebeck coefficient n-Ca₀.₉₇Bi₀.₀₃MnO₃

Fig. 6 and 7 show the electrical resistivity value of the p-type and n-type indicated ceramic behavior in low temperatures and showed semiconductor behavior in high temperatures. The electrical conductivity was decreased with the increasing of temperature and the influence of Bi substitution on the Ca-site of the n-type. Lowest electrical resistivity and an increase in carrier concentration [5] was also apparent and confirmed by the power factor shown.
in Fig. 8. The electrical power of 3 thermoelectric cells was increased when the temperature difference was increased from 1-200 K. The p-type uni-leg demonstrated the lowest power output at around 1.3 mW, which shows it has the effect of high electrical resistivity. However the n-type uni-leg exhibited the highest electrical power output at around 5 mW, because of the substitution of Bi on CaMnO₃. The connected p-n junction power was maximized at around 4 mW because p-type has low power, as shown in Fig. 9. However, the selection method for fabrication should also consider the stability of the cell. The π-shape thermoelectric cell showed good contract and stable total resistivity.

4. Conclusion

It was found that, the XRD of p-type and n-type showed a single phase of compound consistent with PDF# 00-058-0661 and PDF# 00-050-1746, respectively. The n-type uni-leg cell had the highest voltage of 76.8 mV, electrical current of around 70mA, electrical power of 5 mW and a conversion efficiency of 0.187% at a temperature difference of 200K. This cell demonstrates it is the most feasible regarding the fabrication of thermoelectric generators, whilst proving itself the product of a developed method for fabricating high stability cells.
5. References

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