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Thermoelectric Energy Conversion of p–$Ca_3Co_4O_9$/n–$CaMnO_3$ Module

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Abstract

A TE module based on low–temperature difference (ΔT) of 12 pairs of p–$Ca_3Co_4O_9$ /n–$CaMnO_3$ (p–CCO /n–CMO) legs with novelty dimensions of 0.5×5×3 mm^3 was fabricated using low cost of Cu electrodes and ceramic substrates. With a hot–side temperature of the module at 473 K and ΔT of 200 K in air with load resistance of 0.1–0.75 kΩ, the module generated up to an output voltage (V_{out}) of 0.8 V, output current (I_{out}) of 2.46 mA, maximum output power (P_{out}) of 1.98 mW and maximum conversion efficiency (η) of 0.15 %.

Keywords: thermoelectric energy conversion, p–$Ca_3Co_4O_9$/n–$CaMnO_3$ module, novelty TE legs dimension, thermoelectric properties

1. Introduction

Because of global energy and environmental problems, research and development has been promoted in the field of thermoelectric (TE) modules which use heat energy that can be converted directly into electrical energy. Such modules offer alternative energy, low–cost electricity, and green energy technology without the use of moving parts or production of environmentally deleterious wastes [1–2].

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TE modules have been used in military, aerospace, instrument, industrial and commercial products, as power−generation devices for specific purposes. The old TE modules based on Bi_2Te_3 and Sb_2Te_3 provide η of about 4−5% [3] but they are toxic and cannot be used at high temperatures. Several pieces of work have investigated the fabrication, performance and application of oxide−based TE modules such as the p−$Ca_{2.76}Cu_{0.24}Co_4O_9$/$n$−$Ca_{0.8}Dy_{0.2}MnO_3$ [3], p−$Ca_{2.7}Bi_{0.3}Co_4O_9$/ n−$La_{0.9}Bi_{0.1}NiO_3$ [4], p−$Ca_{2.75}Cd_{0.25}Co_4O_9$/$n$−$Ca_{0.92}La_{0.08}MnO_3$ [5], p−$Ca_3Co_4O_9$/ n−$(ZnO)_7In_2O_3$ [6], p−$Ca_3Co_4O_9$/n−$Ca_{0.95}Sm_{0.05}MnO_3$ [7], p−$Ba_{0.2}Sr_{0.8}PbO_3$/n−Li-doped NiO [8], p−$Ca_{2.7}Bi_{0.3}Co_4O_9$/n−$CaMn_{0.98}Mo_{0.02}O_3$ [9]. In this study, we purposed the module using 12 pairs of p−CCO and n−CMO, Cu electrodes, and ceramic substrates for low cost. The TE type, TE properties, power generation and η were measured and analysed. Furthermore, we extracted $CaCO_3$ from environmentally friendly golden apple snail to synthesis CCO and CMO materials by solid state reaction (SSR) method.

2. Materials and Method

2.1. Preparation of Materials and Thermoelectric Properties

The CCO material was obtained by mixing $CaCO_3$ with Co_3O_4, calcined at 1173 K for 12 h and sintered at 1193 K for 24 h in air. The CMO material was prepared by mixing $CaCO_3$ with MnO_2. Polyvinyl acohol was added as a binder with CMO at a ratio of 1 g : 1 mL. Calcination was conducted at 1073 K for 24 h and sintering at 1423 K for 36 h in air. Both bulk materials were cut and polished by using a precision saw and grinder to measure crystal structure (XRD; SHIMUDZU), microstructure (SEM, TEM; JEOL) and TE properties (ZEM3; ULVAC).

2.2. Preparation of Thermoelectric Module

The module was fabricated from p−CCO and n−CMO pairs with dimension of $0.5\times5\times3$ mm^3, using Cu electrodes of 0.05 thickness and ceramic substrate dimensions of $5\times5\times1.0$ mm^3 as shown in Fig. 1. The Cu electrodes were attached on the ceramic plates using epoxy adhesive to achieve electrical conduction. The twelve p−n legs and Cu electrodes on the ceramic substrate were adhered by silver paint. The internal resistance (R_{in}), V_{out} and I_{out} of the module were measured. The maximum P_{out} was calculated by the V_{out} and I_{out}, which were found by changing a small amount of current with a source meter. The heat source T_{hot} had a value of 473 K and ΔT $(T_{hot} - T_{cold})$ of 200 K. The V_{out}, in a close circuit on electrical load condition, can be deduced by the relation $V_{out} = V_0 R_L / (R_{in} + R_L)$ and the I_{out} is given by the relation $I_{out} = V_0 (R_{in} + R_L)$. The module was placed on a hot plate, heated from 273 K to 473 K, and continuously measured to evaluate the efficiency, η. The efficiency, η, is defined as $\eta = I^2 R_L / \dot{Q}_H = I^2 R_L / \mathrm{n} S_{p,n} T_H I + K_{p,n} \Delta T - \frac{1}{2} I^2 R_{in}$ where $\dot{Q}_H$ is heat flow from the source to the sink and the thermal conductance is given by $K_{p,n} = \kappa_p A_p / L_p + \kappa_n A_n / L_n$.

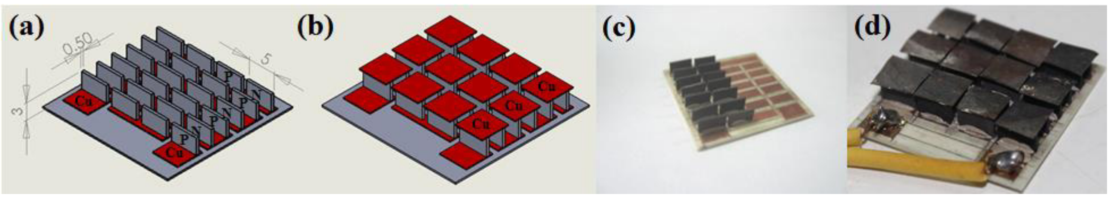

Fig. 1. Schematic diagram of the module (a) *p* and *n* legs input to ceramic substrate, (b) attract Cu electrodes, (c) attract *p* and *n* legs and (d) fabricate TE module

3. Results and Discussion

3.1. Microstructure, Thermoelectric Type and Thermoelectric Properties

Fig. 2(a), (d) show the results of microstructure of CCO and CMO materials of agglomerated powder having sizes of 1−5 µm. The diffraction patterns indicate CCO has orthorhombic structure while CMO has cubic structure, in agreement with the XRD results. The high theoretical densities of 87.52% for CCO and 96.47% for CMO were obtained for both materials.

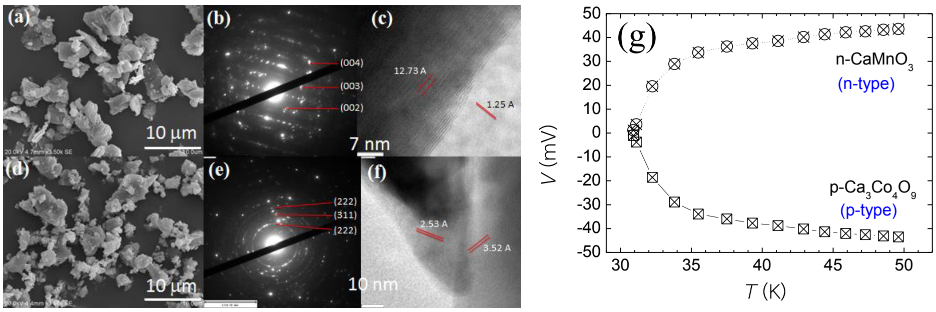

Fig. 2. (a) SEM micrographs of CCO powder, (b) TEM diffraction pattern showing $Ca_3Co_4O_9$ phase, (c) Bright field (BF) image of CCO, (d) SEM micrographs of CMO powder, (e) TEM diffraction pattern showing $CaMnO_3$ phase, (f) BF image of CMO, and (g) V vs T of *p*–CCO/*n*–CMO from hot probe

Fig. 3 (a–b) show results of the electrical resistivity (ρ), Seebeck coefficient (S), thermal conductivity (κ) versus temperature, following the relationship of $ZT = S^2T / \rho\kappa$.

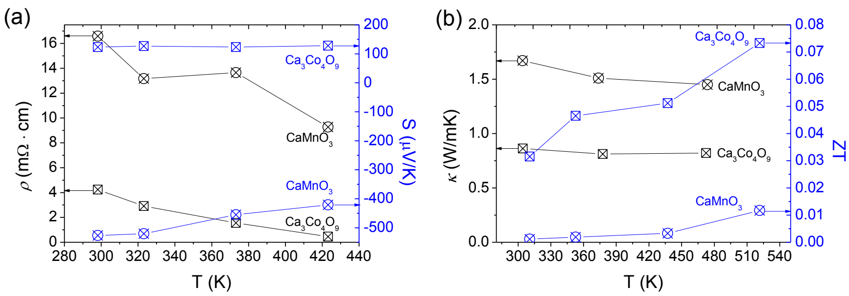

Fig. 3. (a) ρ and S of CCO and CMO materials vs T (b) κ and ZT of CCO and CMO materials vs T

3.2. Thermoelectric Power Generation

Fig. 4(a) shows V_{out} versus I_{out} for the same module and ΔT with different loads of 0.1–0.75 kΩ. Linear relationship obtained enabled V_0 to be calculated (as intercept on y–axis). The estimated V_0 value is 23.03 mV in these temperature conditions. The R_{in} resistance obtained by this method reaches 0.36 kΩ. The inset of Fig. 4 (b) shows the P_{out} curve of this module had a maximum value of 1.98 mW. The theoretical open circuit voltage (V_{cal}) value is given by the relation $V_{cal} = \mathrm{n}(S_p - S_n)(T_{hot} - T_{cold})$, where n is the number of pairs [10]. For the module comprising twelve p–n pairs, $V_{cal} = 1.55$ V was calculated for $(S_p = 123.09\ \mu V/K,\ S_n = -526.79\ \mu V/K,\ T_{hot} - T_{cold} = 200\ K,\ n = 12)$; however, the measured open circuit voltage (V_{open}) of 1.5 V corresponds to only 96.16% of V_{cal} . The results of η versus ΔT are shown in Fig. 4(b) and the η_{max} value is 0.15% at $\Delta T = 200$ K . This low value is due to the high internal and contact resistances of the module which are known to be the main problem for TE module performance. For the manufacturing factor (MF) defined as $MF = R_{ideal} / R_{in}$ [11] where R_{ideal} is the ideal resistance, the results show an MF value of 0.3 in agreement with results shown by Shin W et al. [8].

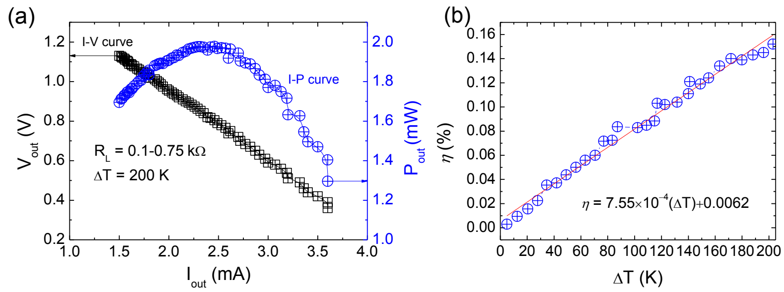

Fig. 4. (a) V_{out} vs I_{out} and P_{out} vs I_{out} and (b) η vs ΔT for difference electrical loads and ΔT of 200 K

4. Conclusion

A TE module, consisting of 12 pairs of p–CCO–Cu electrodes and n–CMO–Cu electrodes on ceramic substrates was fabricated. The maximum P_{out} of TE module under $\Delta T = 200$ K was 1.98 mW and increased with increasing ΔT . The maximum η of 0.15% can make cost-efficient electricity. This work was funded by the Electricity Generating Authority of Thailand (EGAT).

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