Fabrication of a Thermoelectric Module Using p- and n-Type Oxide Thermoelectric Materials

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Abstract

Oxide thermoelectric materials promise better thermoelectric properties for high temperature power generation applications. Within this context, an oxide thermoelectric module with three pairs of p- and n-type thermoelectric materials has been fabricated. $Ca_{2.7}Ag_{0.3}Co_4O_9$ and $Zn_{0.96}Al_{0.02}Ga_{0.02}O$ have been synthesized by sol-gel method and dense bulk samples of them have been produced by cold isostatic pressing at 400 MPa for 10 min for the p- and n-type legs of the thermoelectric module, respectively. To obtain an open circuit voltage, the bottom alumina plate of the thermoelectric (TE) module has been heated to 653 K and the temperature of the top alumina plate has been read as 338 K by a digital thermocouple. The open circuit voltage of the TE module reached to 130 mV under the temperature difference of 315 K.

Key words: Thermoelectric module, sol-gel, Seebeck effect, open circuit voltage.

1. Introduction

Nowadays, a large amount of thermal energy has been being rejected from many industrial processes or similar sources as waste heat at low and high temperatures. Thermoelectric (TE) power generation has become a promising technology to recover waste heat by converting heat directly into electricity [1]. TE devices, used in power generation, are based on Seebeck effect that if the hot ends of p- and n-type materials are electrically connected, an output voltage is produced [2]. Efficiency of a TE material has been evaluated by dimensionless figure of merit (ZT) defined as $ZT = S^2\sigma T/k$, where S is the Seebeck coefficient (μV/K), σ is the electrical conductivity (S/m), T is the temperature (K) and k is the thermal conductivity (W/mK). A TE material should have high Seebeck coefficient and electrical conductivity associated with low thermal conductivity [3].

Over the past two decades, many studies have contributed the literature to obtain high-performance TE materials for energy harvesting applications. The doped alloy TE materials based on Bi_2Te_3 are the best-known ones up to date, and they exhibit a ZT of 1 at ambient temperature [4]. Today, commercially available TE modules are mostly made from intermetallic

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BiTe-based bulk TE materials [5]. Nevertheless, because of being oxidized and vaporized in air, these TE materials are not suitable for high temperature applications. Therefore, oxide TE materials are used instead of these TE materials at high temperatures and in air. Also, TE oxide materials stand out that they have good thermal stability at high temperatures and low toxicity in comparison with conventional intermetallic alloys [4]. For instance, contrary to many state-of-the-art TE materials, ZnO, as an oxide TE material, is environmentally friendly and consists of abundant elements [6].

Investigations on oxide TE materials have shown that Na_xCoO_2 and $Ca_3Co_4O_9$ as p-type and $SrTiO_3$, $CaMnO_3$ and ZnO as n-type have been promising for oxide TE materials [7]. In the meanwhile, considerable theoretical and experimental studies have been performed to increase the thermopower and ZT in cobalt oxides [8]. ZT value of undoped $Ca_3Co_4O_9$ has been specified as 0.3 at 1000 K by Walia et al. [9]. In addition, there have been many studies with different doping materials on $Ca_3Co_4O_9$ to enhance its TE properties. The highest ZT value for polycrystalline $Ca_3Co_4O_9$ as a p-type material has been obtained by Wang et al. with both Ag doping and Ag addition to $Ca_3Co_4O_9$. $Ca_{2.7}Ag_{0.3}Co_4O_9$/Ag-10 wt% composite has shown the best ZT = 0.5 at 1000 K so far [10]. TE properties for undoped and doped ZnO have been reported in various publications so far, and the best ZT for dually doped ZnO with Al and Ga have resulted in 0.65 at 1247 K [6].

TE modules consist of p- and n-type TE materials connected electrically in series and thermally in parallel [4]. There have been studies on fabrication of TE modules and generators in the literature. A brief information about the works performed and open circuit voltages of these studies have been given in discussion section. In this study, a TE module with 3 pairs of p-type $Ca_{2.7}Ag_{0.3}Co_4O_9$ and n-type $Zn_{0.96}Al_{0.02}Ga_{0.02}O$ TE materials has been fabricated and open circuit voltage of the TE module has been evaluated.

2. Materials and Method

In this study, p-type $Ca_{2.7}Ag_{0.3}Co_4O_9$ and n-type $Zn_{0.96}Al_{0.02}Ga_{0.02}O$ TE materials for the legs of TE module were synthesized by sol-gel method. Solution was obtained by mixing the precursors for p- and n-type materials thoroughly in stoichiometric ratios. The solution was mixed at 393 K until the gelation was formed. Then the gel was dried and calcined in air to obtain p- and n-type powders.

The p- and n-type powders were pre-shaped by a mechanical press at 120 MPa and p- and n-type samples were obtained. Next, the samples were subjected to cold isostatic pressing (CIP) at 400 MPa for 10 min for the fabrication of dense bulk materials. After the densification, the bulk samples were treated for 20 h at 1173 K and 10 h at 1673 K for the p- and n-type samples, respectively. Then, the bulk materials were cut into pieces with a cross-sectional area of 4 mm x 5 mm and a height of 12.7 mm for the legs of the TE module.

The TE module was constituted of three pairs of $Ca_{2.7}Ag_{0.3}Co_4O_9$ and $Zn_{0.96}Al_{0.02}Ga_{0.02}O$ for the p- and n-type legs to evaluate heat to electricity performance of the module. Two alumina plates with the dimensions of 12.7 mm wide, 31.7 mm long and 4 mm thick were used as substrates. Ag paste-Ag foil-Ag paste electrodes were formed by using Ag foils with a thickness of 1 mm and Ag paste. The legs and the electrodes were placed between the alumina plates and the module was built. After the assembly, the module was dried at 373 K and treated at 1073 K for 1 h to metallize the electrodes. The module is shown in Figure 1.

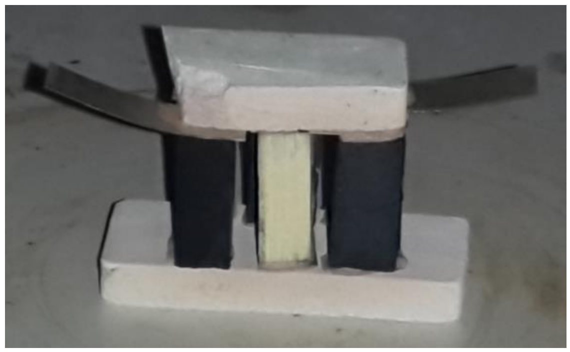

Figure 1. Photograph of the TE module consisting of 3 pairs of p- and n-type legs.

To obtain an open circuit voltage from the TE module, the module was placed on a hot plate and the bottom alumina plate was heated to 653 K. The temperature difference between the hot and cold sides were measured by two digital thermocouples. The open circuit voltage of the module was measured by a digital multimeter.

3. Results and Discussion

Table 1 shows the open circuit voltage (V_O) value for the TE module. When the bottom alumina plate of the TE module was heated to 653 K, the temperature of the top alumina plate was read as 338 K by the digital thermocouple, and a temperature difference (ΔT) of 315 K occurred between the hot and cold sides of the TE module. The open circuit voltage of the TE module reached to 130 mV under ΔT = 315 K.

Table 1. Open circuit voltage (V_O) of the TE module.

Hot Side Temperature (T_H) (K)	Cold Side Temperature (T_C) (K)	ΔT (K)	Open Circuit Voltage (mV)
653	338	315	130

Many researchers have reported open circuit voltages from many types of TE modules as shown in Table 2. Since a comparison between the modules is difficult due to the differences in the number of pairs, dimensions of the p- and n-type legs and ΔT, we have tried to compare the open circuit voltage of the TE module to that of other oxide-based TE modules fabricated until now. The studies have been sorted according to the ΔT between the hot and cold side temperatures since thermoelectricity is directly related to the temperature difference.

It seems that 988 mV V_O of the module of the Reference [11] with 8 pairs of p- and n-type legs is bigger than the 130 mV V_O of this work. The reason for this higher V_O may be that they have operated the module at a higher hot side temperature of 1046 K. The 100 mV and 194 mV V_O of the modules of the References [14] and [20] with both 1 pair of legs appear to be closer to the 130 mV V_O of this work. Although the numbers of leg pairs are lower than this work, they have also operated the modules at higher temperature differences of 500 K and 727 K and hot side temperatures of 1073 K and 1175 K, respectively.

Table 2. Open circuit voltages for reported TE modules.

Reference	Materials	Number of Pairs	Leg Size (mm)	T_H (K)	ΔT (K)	V_O (mV)
This work	**P-type $Ca_{2.7}Ag_{0.3}Co_4O_9$ N-type $Zn_{0.96}Al_{0.02}Ga_{0.02}O$**	**3**	**4x5x12.7**	**653**	**315**	**130**
[11]	P-type $Ca_{2.75}Gd_{0.25}Co_4O_9$ N-type $Ca_{0.92}La_{0.08}MnO_3$	8	3x3x25	1046	390	988
[12]	P-type $NaCo_2O_4$ N-type $Zn_{0.98}Al_{0.02}O$	12	3x4x10	839	462	780
[13]	P-type $Ca_3Co_4O_9$ N-type $Zn_{0.98}Al_{0.02}O$	8	3x3x8	906	496	700
[14]	P-type $Ca_{2.7}Bi_{0.3}Co_4O_9$ N-type $La_{0.9}Bi_{0.1}NiO_3$	1	3.7x4-4.5x4.7	1073	500	100
[15]	P-type $GdCo_{0.95}Ni_{0.05}O_3$ N-type $CaMn_{0.98}Nb_{0.02}O_3$	2	4x4x5	800	500	340
[16]	P-type $Ca_3Co_4O_9$ N-type $Ca_{0.98}Sm_{0.02}MnO_3$	2	3x6x6	873	523	328
[17]	P-type $Ca_{2.7}Bi_{0.3}Co_4O_9$ N-type $Ca_{0.98}Sm_{0.02}MnO_3$	2	3x6x6	873	525	360
[18]	P-type $Ca_{2.7}Bi_{0.3}Co_4O_9$ N-type $La_{0.9}Bi_{0.1}NiO_3$	140	1.3x1.3x5	1072	551	4500
[19]	P-type $Ca_3Co_4O_9$ N-type $Ca_{0.95}Sm_{0.05}MnO_3$	2	4x4x10	990	630	400
[20]	P-type $Ca_3Co_4O_9$ N-type $Ca_{0.9}Nd_{0.1}MnO_3$	1	8.5x6x8.5	1175	727	194
[21]	P-type $Ca_{2.7}Bi_{0.3}Co_4O_9$ N-type $CaMn_{0.98}Mo_{0.02}O_3$	8	5x5x4.5	1273	975	700

Conclusions

An oxide-based TE module consisting of three pairs of p-type $Ca_{2.7}Ag_{0.3}Co_4O_9$ and n-type $Zn_{0.96}Al_{0.02}Ga_{0.02}O$ materials has been successfully fabricated. P- and n-type powders have been synthesized by sol-gel method and the bulk samples were densified by CIP. The module can generate an open circuit voltage of 130 mV with a hot-side temperature of 653 K and a temperature difference of 315 K. Since the V_O of the other studies in the literature is higher than the V_O of this work, the TE module should be operated at higher hot-side temperatures and temperature differences.

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