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Fabrication of Thermoelectric Module from Efficient Earth Abundant Thermoelectric Materials

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Abstract

To develop a power generation technology, we proposed low-cost and nontoxic earth abundant thermoelectric materials consisting of n-type and p-type iron oxides. For high temperature applications of power generation, thermoelectric materials consisting of oxide assure better thermoelectric properties. In this research work, thermoelectric module has been fabricated with three pairs of p-type and n-type thermoelectric materials. In this context, we used Hematite (α-Fe_2O_3) as thermoelectric material which is naturally n-type. By doping Zn, α-Fe_2O_3 turned into p-type. Using spin coating method, n-type α-Fe_2O_3 and p-type Zn doped α-Fe_2O_3 (Zn:α-Fe_2O_3) have been synthesized. For the p-type and n-type legs of the thermoelectric module, the dense bulk samples of α-Fe_2O_3 have been produced by cold isostatic pressing at 450 MPa for 15 min. Six-leg thermoelectric module consisting of three pairs of n-type α-Fe_2O_3 and p-type Zn:α-Fe_2O_3 bulks of 3×5 mm^2 cross-section and heights of 10.5 mm were fabricated. At an operating temperature of 893 K with a temperature difference of 471 K, an open circuit voltage of 744 mV was generated.

Keywords: Thermoelectric Module, Hematite, Spin Coating Method, Open Circuit Voltage

1. Introduction

At the present time, at low and high temperatures, from many industrial processes or alike sources have been being discarded a large amount of thermal energy as waste heat. For future generations, the rapid decreasing of natural resources has led to a flow of research to find the alternative ways of generating energy. More than 50% is wasted in any energy production or conversion process in various forms, for the most part as heat [1]. The processes of converting waste heat into useful energy can reduce the demand for natural resources and also avail us economically. A quite promising technology to recover waste heat by converting heat energy directly into useful electrical energy i.e. electricity which is called a thermoelectric power generation [2]. Since solid state components have no moving mechanical parts, thermal power modules are highly reliable in converting heat energy into electrical energy.

Traditionally thermoelectric modules were made using thermoelectric materials such as Bi_2Te_3, PbTe, SiGe, etc. [3-4]. From conventional materials, the manufacture of thermoelectric modules are well established and commercially widely available. Based on oxide materials, recently the fabrication of modules has emerged and there exist very few reports, particularly on their performance [5–9]. The oxide nature of the thermoelectric material and the operation specifications associated with very high temperatures make it a difficult task and very different from conventional thermoelectric modules. Recent developments in oxide thermoelectric materials have opened up opportunities for the creation of thermoelectric modules that can operate at temperatures up to 1300 K with improved performance by exhibiting good Seebeck coefficients [10-12]. In power generation, thermoelectric devices which are based on Seebeck effect that an output voltage is produced if the hot ends of p-type and n-type materials are electrically connected [13].

The 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) helps to evaluate the efficiency of a thermoelectric material. High Seebeck coefficient and electrical conductivity associated with low thermal conductivity should have present in thermoelectric material which show the better performance [14]. Based on Bi_2Te_3, the doped alloy thermoelectric materials are the most popular up to date and they exhibit the value of dimensionless figure of merit, ZT is 1 at ambient temperature [15].

Commercially, at present, by using intermetallic BiTe-based bulk thermoelectric materials in most cases the available thermoelectric modules are made [16]. However, these thermoelectric materials are not suitable for high temperature application, due to oxidation and volatilization in the air. Therefore, instead of these thermoelectric materials, at high temperatures and in air, the oxide thermoelectric materials are used because at high temperatures and low toxicity in comparison with conventional intermetallic alloys, they have good thermal stability [15]. For instance, α-Fe_2O_3 is environmentally friendly and consists of abundant elements.

In this research work, based on bulk materials of α-Fe_2O_3 and Zn:α-Fe_2O_3, we construct and describe the fabrication of thermoelectric modules. Using silver paste, the modules were assembled. So that the thermoelectric elements are electrically connected in series by silver strips and in parallel thermally [17]. Here, the thermoelectric module based on bulk materials of α-Fe_2O_3 and Zn:α-Fe_2O_3 has been fabricated and also open circuit voltage of the thermoelectric module has been evaluated.

2. Materials and Method

Hematite (α-Fe_2O_3) is naturally n-type material. For the need of p-type material, Zn from Zinc acetate ($Zn(CH_3COO)_2.2H_2O$) was doped with α-Fe_2O_3 which make the Zn doped α-Fe_2O_3 (Zn:α-Fe_2O_3) material. In this study, n-type α-Fe_2O_3 and p-type Zn:α-Fe_2O_3 thermoelectric materials for the legs of thermoelectric module were synthesized by spin coating method. In stoichiometric ratios, the required solution was obtained by mixing the precursors for n-type and p-type materials thoroughly. The required solutions were mixed and stirred at 25 minutes properly. Then the mixtures were annealed at 673 K for 4 hours to get the powder form. Then this powders of α-Fe_2O_3 and Zn doped α-Fe_2O_3 give the n-type and p-type powders, respectively.

For obtaining p-type and n-type samples, by a mechanical press at 120 MPa, the p-type and n-type powders were pre-shaped. For the fabrication of dense bulk materials, then the samples were subjected to cold isostatic pressing (CIP) at 450 MPa for 15 min. After the densification, for the p-type and n-type samples, the bulk samples were treated for 19 h at 1063 K and 9.5 h at 1597 K, respectively. Then, the bulk materials were cut into pieces with a cross-sectional area of 3 mm × 5 mm and a height of 10.5 mm for the legs of the thermoelectric module. A typical schematic diagram of a module is shown in Figure 1. To evaluate heat to electricity performance of the module, the thermoelectric module was constituted of three pairs of α-Fe_2O_3 and Zn doped α-Fe_2O_3 for the p-type and n-type legs. Two alumina plates were used as substrate.

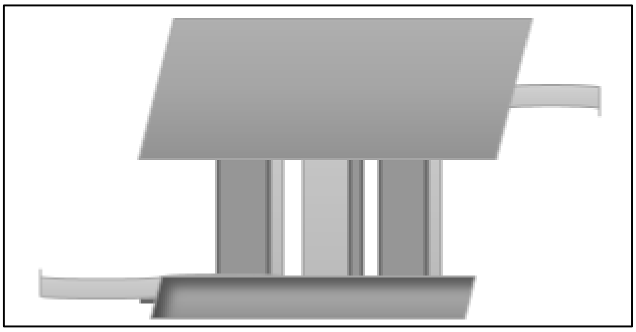

Figure 1: A typical schematic diagram of a thermoelectric module.

The dimensions of alumina plates were 11.5 mm wide, 29.5 mm long and 3.8 mm thick. Between the alumina plates, the legs and the electrodes were placed then the module was built. After the construction of the module, to metallize the electrodes, the module was dried at 423 K and treated at 1143 K for 1.5 hour.

To get an open circuit voltage from the thermoelectric module, the module was placed on a hot plate and the bottom alumina plate was heated to 893 K. By two digital thermocouples, the temperature difference between the hot and cold sides of the thermoelectric module were measured. By using a digital multimeter, the open circuit voltage of the thermoelectric module was also measured.

3. Result and Discussion

When the thermoelectric module was heated to 893 K in the bottom alumina plate then the temperature of the top alumina plate was read as 338 K by the digital thermocouple. That's why, between the hot and cold sides of the thermoelectric module, a temperature difference of 471 K was occurred. Under the temperature difference 471 K, the open circuit voltage of the thermoelectric module come at 744 mV. The value of open circuit voltage for the thermoelectric module is shown in Table 1.

Table 1: The open circuit voltage of the thermoelectric module for this work.

Temperature in Hot Side (K)	Temperature in Cold Side (K)	Temperature Difference (K)	Open Circuit Voltage (mV)
893	422	471	744

The open circuit voltages of different materials of thermoelectric modules which are reported in researchers which is shown in Table 2. It is seen from the Table 2 that, due to the differences in the number of pairs, dimensions of the p-type and n-type legs and temperature difference, a comparison between the modules is difficult but tried to compare the open circuit voltage of the thermoelectric module to that of other thermoelectric modules fabricated so far. From references mentioned in Table 2, it is seen that, depending on the dimensions of the p-type and n-type legs, number of pairs and temperature difference, open circuit voltages changed with different operating temperatures.

Table 2: The open circuit voltages of different materials of thermoelectric modules.

Materials	Leg Size (mm)	No. of pairs	Temperature in Hot Side (K)	Temperature Difference (K)	Open Ckt. Voltage (mV)	Reference
P-type Zn:α-Fe_2O_3 N-type α-Fe_2O_3	3×5×10.5	3	893	471	744	This research work
P-type $Ca_3Co_4O_9$ N-type $Zn_{0.98}Al_{0.02}O$	3×3×8	8	906	496	700	[18]
P-type $NaCo_2O_4$ N-type $Zn_{0.98}Al_{0.02}O$	3×4×10	12	839	462	780	[19]
P-type $Ca_{2.7}Ag_{0.3}Co_4O_9$ N-type $Zn_{0.96}Al_{0.02}Ga_{0.02}O$	4×5×12.7	3	653	315	130	[17]
P-type $Ca_{2.7}Bi_{0.3}Co_4O_9$ N-type $CaMn_{0.98}Mo_{0.02}O_3$	5×5×4.5	8	1273	975	700	[20]
P-type $Ca_3Co_4O_9$ N-type $Ca_{0.9}Nd_{0.1}MnO_3$	8.5×6×8.5	1	1175	727	194	[21]
P-type $Ca_{2.7}Bi_{0.3}Co_4O_9$ N-type $La_{0.9}Bi_{0.1}NiO_3$	1.3×1.3×5	140	1072	551	4500	[22]
P-type $Ca_{2.7}Bi_{0.3}Co_4O_9$ N-type $Ca_{0.98}Sm_{0.02}MnO_3$	3×6×6	2	873	525	360	[23]
P-type $Ca_3Co_4O_9$ N-type $Ca_{0.95}Sm_{0.05}MnO_3$	4×4×10	2	990	630	400	[24]
P-type $Ca_3Co_4O_9$ N-type $Ca_{0.98}Sm_{0.02}MnO_3$	3×6×6	2	873	523	328	[25]
P-type $GdCo_{0.95}Ni_{0.05}O_3$ N-type $CaMn_{0.98}Nb_{0.02}O_3$	4×4×5	2	800	500	340	[26]
P-type $Ca_{2.75}Gd_{0.25}Co_4O_9$ N-type $Ca_{0.92}La_{0.08}MnO_3$	3×3×25	8	1046	390	988	[5]
P-type $Ca_{2.7}Bi_{0.3}Co_4O_9$ N-type $La_{0.9}Bi_{0.1}NiO_3$	3.7×4×4.7	1	1073	500	100	[9]

4. Conclusion

In this research, a thermoelectric module has been successfully fabricated which consisting of three pairs of n-type α-Fe_2O_3 and p-type Zn doped α-Fe_2O_3 materials. By using spin coating method, n-type α-Fe_2O_3 and p-type Zn doped α-Fe_2O_3 materials have been synthesized. The bulk samples of those materials were densified by cold isostatic pressing. With a temperature in hot side of 893 K and a temperature difference of 471 K, the thermoelectric module can generate an open circuit voltage of 744 mV.

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