THERMOELECTRIC ENERGY USING LOCAL MINERALS p-Fe_2O_3-SO_3-SiO_2-others and n-MnO-Fe_2O_3-SiO_2-BaO-others

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ABSTRACT

Thermoelectric generator consists of mineral bulks p-Fe_2O_3-SO_3-SiO_2-others (S = 0.09 mV/K, ρ = 47.2 Ω·m, κ = 130.9 W/m·K, $P \sim 10^{-10}$ W/m·K^2, $Z \sim 10^{-12}$ K^{-1}) and n-MnO-Fe_2O_3-SiO_2-BaO-others (S = –0.83 mV/K, ρ = 797.9 Ω·m, κ = 69.6 W/m·K, $P \sim 10^{-10}$ W/m·K^2, $Z \sim 10^{-11}$ K^{-1}) with 0.5×0.5 cm^2 cross-sectional area and 1.0 cm height. Both of the types connected electrically in series and thermally in parallel on printed circuit board for a cold side (T_C), copper sheets for connection between p-legs and n-legs using silver paste, mica plate with thermal conductive silicone for a hot side (T_H), and electrical wires for connection to an electric meter. For preliminary test in air at room temperature indicated that the open circuit voltage (V_O) and short circuit current (I_S) increased with increasing temperature difference (ΔT), while the internal resistance (R_I) decreased. Thermoelectric generator of twenty pairs can be provided the V_O and I_S up to 495.2 mV and 3.52 μA, while the R_I reached a value of 1.92 MΩ for ΔT = 173.5 K (T_H = 513.3 K and T_C = 339.8 K).

KEYWORDS: *Thermoelectric energy, p-Fe_2O_3-SO_3-SiO_2-others, n -MnO-Fe_2O_3-SiO_2-BaO-others*

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INTRODUCTION

Since the year 2013-1015, thermoelectric minerals have been found in Loei Province, which is located in the northeastern part of Thailand. Mineral specimens were thermoelectric compound of the p-type (Fe_2O_3-SO_3-SiO_2-others, Fe_2O_3-SO_3-MgO-others, SiO_2-Fe_2O_3-CaO-others, SO_3-CaO-SiO_2-others) and n-type (Fe_2O_3-SiO_2-CuO-others, BaO-K_2O-SiO_2-others, MnO-Fe_2O_3-SiO_2-BaO-others) [1-9].

Recently, Dawongsa et al. reported that a thermoelectric generator made from twenty pairs of p-Fe_2O_3-SO_3-SiO_2-others and n-Fe_2O_3-SiO_2-CuO-others mineral bulks. It can be generated the open circuit voltage and short circuit current up to 71.7 mV and 0.08 μA for a temperature difference of 38 K in air at room temperature, respectively [10].

In this research, local minerals p-Fe_2O_3-SO_3-SiO_2-others and n-MnO-Fe_2O_3-SiO_2-BaO-others were prepared in the powder and bulk forms. Analysis of the chemical composition and phase formation, determination of the thermoelectric property and efficiency, fabrication and test of a thermoelectric generator at room temperature are investigated and presented.

MATERIALS AND METHODS

Fabrication flow chart for the preparation of local mineral specimens is shown in Fig. 1. Mineral samples were crushed and calcined at 373 K in air for 3 h. Calcined powders were crushed and mixed with polyvinyl alcohol (PVA) in 5 g : 1 mL ratio and annealed at 373 K in air for 1 h. Annealed powders were crushed and pressed into bulk solids at the pressure of 200 kg/cm^2 in air before subjected to sintering stage. Bulk precursors were sintered at 473 K in air for 3 h. Subsequently, sintered bulks were cut and polished to determine thermoelectric properties and efficiencies. Mineral specimens, powder and bulk samples are shown in Fig. 2.

Chemical composition and phase formation of powder samples were analyzed using the x-ray fluorescence (Philips PW-2404) and x-ray diffraction (Shimadzu XRD-6100) at National Metal and Materials Technology Center and Thermoelectric Research Center, Sakon Nakhon Rajabhat University, respectively. Thermoelectric properties and efficiencies of bulk samples were determined by the experimental set up at Science Center, Loei Rajabhat University, which were already calibrated by testing with solid copper (Cu) of 8.95 g/cm^3 density.

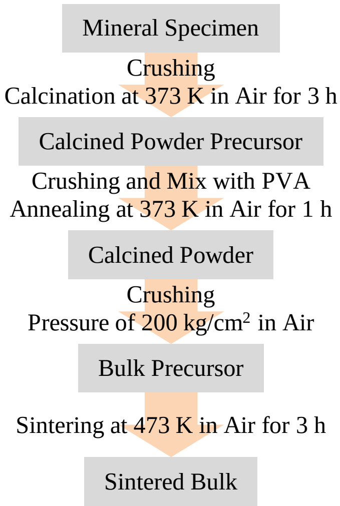

Fig. 1. Preparation of local mineral specimens

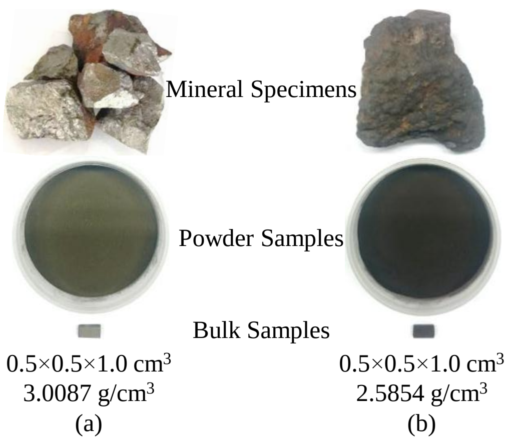

Fig. 2. Mineral specimens, powder and bulk samples (a) Fe_2O_3-SO_3-SiO_2-others and (b) MnO-Fe_2O_3-SiO_2-BaO-others

Hot probe experiment was used to determine the type of charge carrier and Seebeck coefficient (S) as shown in Fig. 3. The hot and cold sides between across two ends of a bulk sample are connected to a digital multimeter. The hot and low temperatures are sensed by the type K thermocouples, which connected to the digital thermometers. A ceramic resistor was placed on hot side to heat by applying current using a direct current power supply. Cold side was surrounded by air at room temperature. The S was determined from the relation between thermoelectric voltage (ΔV) and temperature difference (ΔT), which is given by $S = \Delta V/\Delta T$ [11-13].

Current-voltage characteristics measurement was used to evaluate the electrical resistivity (ρ) as shown in Fig. 4. The current (I) and voltage (V) were applied using a direct current power supply and measured by the digital multimeters. The ρ can be estimated from $\rho = RA/l$, where R is the resistance ($R = V/I$), A and l are the cross-sectional area and length of a bulk sample, respectively [14-16].

Steady state technique was used to appraise the thermal conductivity (κ) as shown in Fig. 5. The rate of heat flow through a homogenous solid or heat transfer per unit time (dQ/dt) between two ends of solid is directly proportional to the cross-sectional surface area (A) and the temperature gradient (dT/dx) along the path of the heat flow which can be given by the Fourier's law of heat conduction, $\Phi_Q = \kappa(dT/dx)$, where Φ_Q is the heat flux density $(dQ/dt)/A$) [12,17,18].

Thermoelectric efficiencies can be examined from the material's electrical power factor (P) and thermoelectric figure of merit (Z). That can be calculated from the physical parameters S, ρ and κ by using the equations $P = S^2/\rho$ and $Z = S^2/\rho\kappa$, respectively [12,13,19].

Thermoelectric generator was fabricated by using mineral bulks p-Fe_2O_3-SO_3-SiO_2-others and n-MnO-Fe_2O_3-SiO_2-BaO-others with 0.5×0.5 cm^2 cross-sectional area and 1.0 cm height. Both of the types (p-leg and n-leg) connected electrically in series and thermally in parallel on printed circuit board (6.0×10.0 cm^2) for a cold side, copper sheets (0.5×1.5 cm^2, 0.05 cm thickness) for connection between p-legs and n-legs using silver paste, mica plate (5.0×10.0 cm^2, 0.1 cm thickness) with thermal conductive silicone for a hot side, and electrical wires for connection to an electric meter, as shown in Fig. 6.

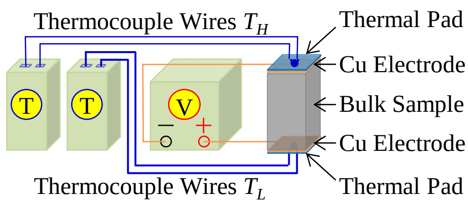

Fig. 3. Experimental set up of thermoelectric sensitivity

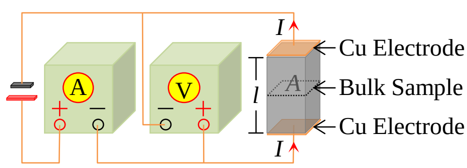

Fig. 4. Experimental set up of electrical resistivity

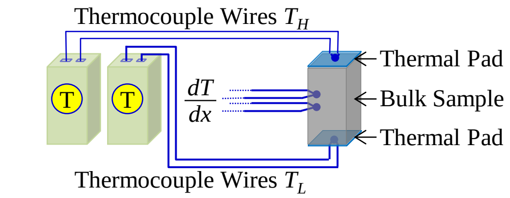

Fig. 5. Experimental set up of thermal conductivity

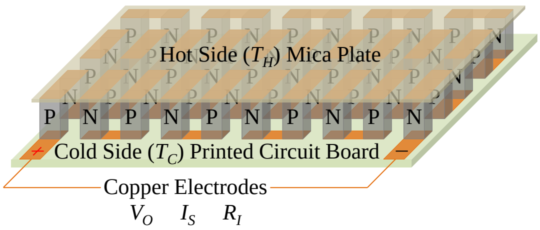

Fig. 6. Fabrication of a thermoelectric generator

RESULTS AND DISCUSSION

Analysis of chemical composition used XRF. The concentration (Conc.) and compounds of the local minerals in Fig. 2(a) and (b) are given in Table 1. From this table found that the mineral specimens included iron (III) oxide (Fe_2O_3 71.03%), Sulfur trioxide (SO_3 22.38%), silicon dioxide (SiO_2 4.21%), others. and manganese oxide (MnO 59.65%), iron (III) oxide (Fe_2O_3 18.35%), silicon dioxide (SiO_2 11.15%), barium oxide (BaO 7.51%), others.

Table 1. Chemical composition of mineral powders

Compounds	Conc. (%)	Compounds	Conc. (%)
Fe_2O_3	71.03	MnO	59.65
SO_3	22.38	Fe_2O_3	18.35
SiO_2	4.21	SiO_2	11.15
Al_2O_3	0.72	BaO	7.51
CaO	0.42	Al_2O_3	1.15
As_2O_3	0.32	TiO_2	0.51
MgO	0.25	K_2O	0.40
Co_2O_3	0.23	CaO	0.31
MnO	0.13	MgO	0.27
K_2O	0.11	ZnO	0.23
Na_2O	0.04	SO_3	0.13
TiO_2	0.04	P_2O_5	0.12
CuO	0.03	Na_2O	0.11
		SrO	0.11

Phase formation analyzed from XRD technique and obtained from the International Centre for Diffraction Data (PCPDFWIN Copyright © JCPDS-ICDD 2003). XRD patterns are shown in Fig. 7. From this figure exhibited that the phases of compounds (PDF # Number) were detected such as Fig. 7(a) Fe_2O_3 (88-2359, 89-7047), SO_3 (73-2169,), SiO_2 (89-1813, 89-5416, 89-7499) and Fig. 7(b) MnO (04-0326, 89-8934), Fe_2O_3 (76-1821, 89-7047), SiO_2 (89-5416, 89-8934), BaO (01-0746).

XRF and XRD results indicated that the mineral powders comprised the Fe_2O_3-SO_3-SiO_2-others and MnO-Fe_2O_3-SiO_2-BaO-others.

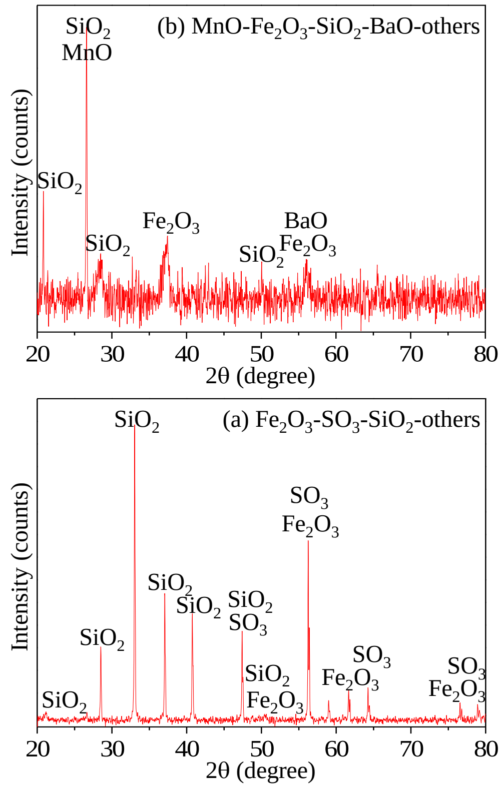

Fig. 7. XRD pattern of mineral powders

Determination results of the thermoelectric property and efficiency of the mineral bulks in air at room temperature are as follows.

Charge carrier and Seebeck coefficient were determined by hot probe experiment as shown in Fig. 8. It was found that Fe_2O_3-SO_3-SiO_2-others showed p-type conduction with S = 0.09 mV/K, while MnO-Fe_2O_3-SiO_2-BaO-others was n-type with S = –0.83 mV/K.

Evaluating electrical resistivity from current-voltage characteristics is shown in Fig. 9. Results exhibited that the ρ values of p-type and n-type are 47.2 Ω·m and 797.9 Ω·m, respectively.

Thermal conductivity was appraised using standard steady state technique as shown in Fig. 10. The κ values of 130.9 W/m·K for p-type and 69.6 W/m·K for n-type were obtained.

Results of calculating electrical power factor and thermoelectric figure of merit gave the values of $P \sim 10^{-10}$ W/m·K^2, $Z \sim 10^{-12}$ K^{-1} for p-type and $P \sim 10^{-10}$ W/m·K^2, $Z \sim 10^{-11}$ K^{-1} for n-type.

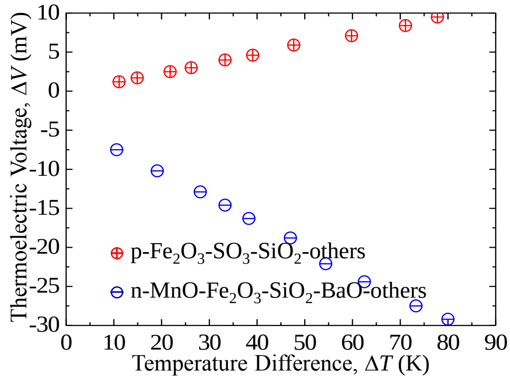

Fig. 8. Thermoelectric voltage as a function of the temperature difference

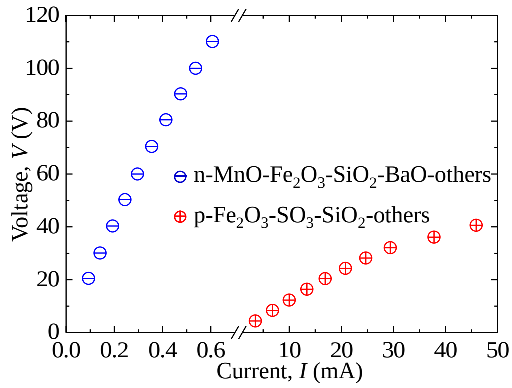

Fig. 9. Current-voltage characteristics for measuring electrical resistivity

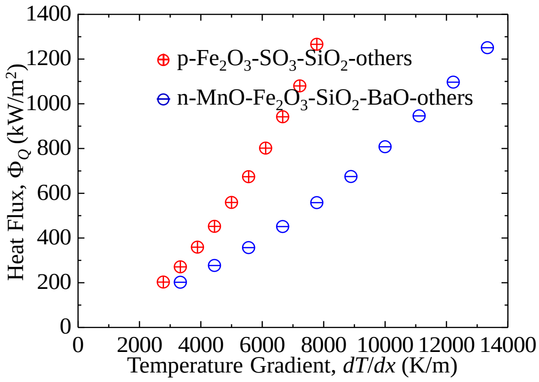

Fig. 10. Heat flux density as a function of the temperature gradient

Testing a thermoelectric generator (TEG) in air at room temperature revealed that the open circuit voltage and short circuit current increased with increasing temperature difference, while the internal resistance decreased. For ΔT = 173.5 K (T_H = 513.3 K, T_C = 339.8 K), the V_O, I_S and R_I are as follows (see Fig. 11).

TEG of 5 pairs provided the V_O and I_S up to 110.9 mV and 2.27 µA while the R_I reached a value of 0.39 MΩ.

TEG of 10 pairs provided the V_O and I_S up to 254.2 mV and 3.10 µA while the R_I reached a value of 0.91 MΩ.

TEG of 15 pairs provided the V_O and I_S up to 375.4 mV and 3.43 µA while the R_I reached a value of 1.39 MΩ.

TEG of 20 pairs provided the V_O and I_S up to 494.2 mV and 3.52 µA while the R_I reached a value of 1.92 MΩ.

TEG of 25 pairs provided the V_O and I_S up to 492.6 mV and 1.04 µA while the R_I reached a value of 2.41 MΩ.

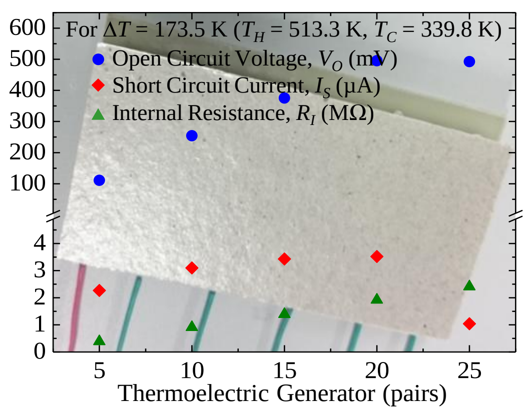

Fig. 11. Test results of a thermoelectric generator

CONCLUSION

Local minerals of p-Fe_2O_3-SO_3-SiO_2-others and n-MnO-Fe_2O_3-SiO_2-BaO-others were used to fabricate a thermoelectric generator. Test results in air at room temperature demonstrated that this device can be provided the thermoelectric energy. However, the high internal resistance was barrier of generating electricity. Decreasing resistance between ohmic contacts and thermoelectric cells are expected to be one of the candidates for good electricity generation. Moreover, the search for new materials with high performance is interested and considered. This will be further investigated.

ACKNOWLEDGEMENTS

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