Thermoelectric Generator Using Local Mineral $MnO\text{-}Fe_2O_3\text{-}SiO_2\text{-}BaO\text{-}Al_2O_3$-Others

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***Abstract*—MnO-Fe2O3-SiO2-BaO-Al2O3-others mineral has been found in Loei Province, Thailand, and was prepared in bulk solid form for determining thermoelectric properties and efficiencies. Charge carrier type and Seebeck coefficient were measured by hot probe method. Electrical resistivity can be estimated from current and voltage characteristics. Steady state technique is used to find thermal conductivity. Power factor and figure of merit were calculated. Results of Determinations at room temperature in air found that a bulk sample (0.30 cm width, 0.40 cm length, 2.00 cm height and 2.63 g/cm3 density) showed n-type material. Seebeck coefficient, electrical resistivity and thermal conductivity were about –10–3 V/K, 103 Ω·m, and 102 W/m·K, respectively. Power factor of ~10–9 W/m·K2 and figure of merit of ~10–11 K–1 were obtained. Making thermoelectric generator coposed of ten bulks, which connected electrically in series but thermally in parallel. Preliminary test indicated that the open circuit voltage increased with increasing temperature difference from 9.3 mV at 9 K up to 66.0 mV at 88 K. While the internal resistance decreased from 14.9 MΩ to 4.5 MΩ. This test demonstrated that a built generator can be generated the electricity. Therefore, it can be used as an important platform for further research and development of thermoelectric technology.**

***Index Terms* —$MnO\text{-}Fe_2O_3\text{-}SiO_2\text{-}BaO\text{-}Al_2O_3$, thermoelectric properties and efficiencies, thermoelectric generator**

I. Introduction

Thermoelectric materials can directly convert thermal energy into electricity, and it can change electrical energy into heat and cold, which have been widely investigated. Good thermoelectric materials depend on their property such as the Seebeck coefficient (S) [1], [2], [3], electrical resistivity (ρ) [4], [5], [6], and thermal conductivity (κ) [7], [8], [9]. The efficiency can be calculated from the physical parameters S, ρ and κ, which is employed and given by the thermoelectric figure of merit $Z = S^2/\rho\kappa$, where S^2/ρ is referred to as the electrical power factor. The development of materials will include the high S, low ρ and κ, which lead to the large Z. Besides, the thermoelectric performance of materials is usually characterized in terms of their dimensionless figure of merit ZT, where T is the absolute temperature. Namely, the large ZT values will be leaded to the high efficiency. However, only those materials which possess a $ZT > 0.5$ are usually regarded as thermoelectric materials [3]. For the Z values of metals, semiconductors, and insulators were about 3×10^{-6} K^{-1}, 2×10^{-3} K^{-1}, and 5×10^{-17} K^{-1} at 300 K, respectively [10].

The search for thermoelectric materials with high efficiency is important that the metal oxide compounds were interested. In this work, $MnO\text{-}Fe_2O_3\text{-}SiO_2\text{-}BaO\text{-}Al_2O_3$-others mineral has been found at Ban Chiang Klom, Tambon Chiang Klom, Amphoe Pak Chom, which is located in the northern part of Loei Province, northeastern Thailand. A local mineral was prepared in bulk solid form. Determining thermoelectric properties and efficiencies such as the type of charge carrier, Seebeck coefficient, electrical resistivity, thermal conductivity, electrical power factor and thermoelectric figure of merit were investigated. Making and testing thermoelectric generator were reported.

II. Experimental Procederes

A. Preparation and Characterizations of Samples

Fabrication flow chart for the preparation of mineral samples is shown in Fig. 1. A mineral specimen was crushed and calcined at 373 K in air for 3 h. Calcined powder precursor was crushed and mixed with PVA (polyvinyl alcohol) in 1 g : 1 mL ratio and annealed at 373 K in air for 1 h. Calcined powder was crushed and pressed into a bulk precursor at the pressure of 200 kg/cm^2 in air before subjected to sintering stage. Bulk precursor was sintered at 473 K in air for 3 h. Subsequently, sintered bulk was cut and polished for determining thermoelectric properties and making thermoelectric generator. Mineral specimen, powder and bulk samples are shown in Fig. 2. Dimension and density of bulk sample are 0.30 cm width, 0.40 cm length, 2.00 height and 2.63 g/cm^3 density.

Chemical composition and phase identification of the mineral samples were analyzed using X-ray fluorescence spectrometry (Philips PW-2404) at National Metal and Materials Technology Center (MTEC) and X-ray diffractometer (Shimadzu XRD-6100) at Thermoelectric Research Center (TRC), Thailand, respectively.

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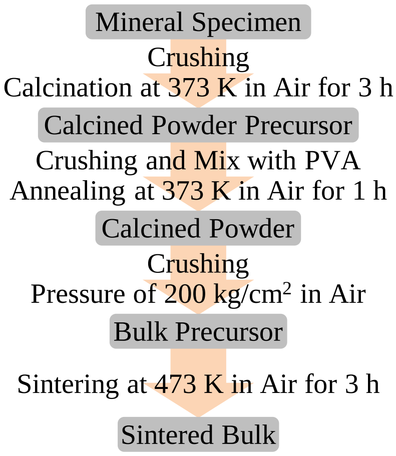

Figure 1. Preparation of powder and bulk samples

Figure 2. Mineral specimen, powder and bulk samples

B. *Determination of Properties and Efficiencies*

Determination of thermoelectric properties included the type of charge carrier, Seebeck coefficient, electrical resistivity, and thermal conductivity at room temperature (T_{room}) in air. The details and experimental setups can be elucidated as follows.

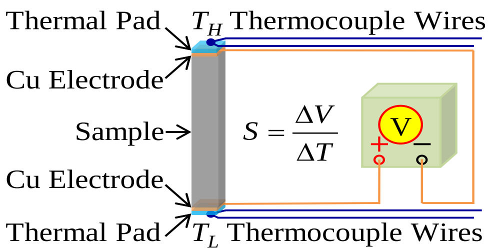

Figure 3. Experimental setup of thermoelectric sensitivity

Type of charge carrier was measured by the hot probe method as shown in Fig. 3. The hot and cold junctions between the across two ends of the sample are connected to the voltmeter. The hot (T_H) and cold (T_L) temperatures are sensed by the type K thermocouples. Ceramic resistor was used to heat the hot junction by applying currents to a resistor placed on the hot side using power supply. The cold junction was surrounded by air at room temperature. Seebeck coefficient (S) can be considered from the relation between thermoelectric voltage (ΔV) and temperature difference ($\Delta T = T_H - T_L$), as in (1) [1], [2], [3].

$$S = \frac{\Delta V}{\Delta T} \tag{1}$$

Electrical resistivity (ρ) can be estimated from current (I) and voltage (V) characteristics as shown in Fig. 4. The power supply was used by applying currents to the sample. The I and V are measured to calculated the ρ in (2), where A and l are the cross-sectional area and length of the sample, respectively [4].

$$\rho = \left[\frac{V}{I}\right]\left[\frac{A}{l}\right] \tag{2}$$

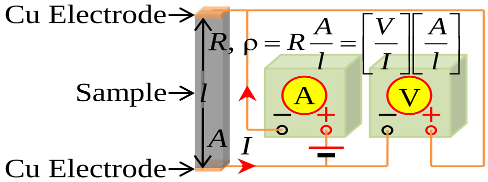

Figure 4. Experimental setup of electrical characteristics

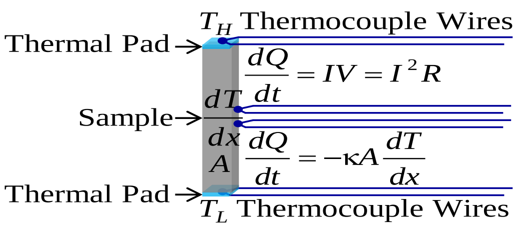

Figure 5. Experimental setup of thermal conductivity

The steady state technique is used to find the thermal conductivity (κ) as shown in Fig. 5. The heat flow rate (dQ/dt) between two ends of the sample can be given in (3) [7], [8], [9], where $dQ/dt = IV = I^2R$ is directly proportional to the cross-sectional area A. The I and V is current and voltage to the resistance R, which was used to heat the hot junction by applying currents to a resistor placed on the hot side using power supply. dT/dx is the temperature gradient along the path of the heat flow. The T_H, T_L, and dT are sensed by the type K thermocouples.

$$\frac{dQ}{dt} = -\kappa A\frac{dT}{dx} \tag{3}$$

The thermoelectric efficiencies can be examined from the electrical power factor (P) and thermoelectric figure of merit (Z), as in (4) and (5) [3], respectively.

$$P = \frac{S^2}{\rho} \tag{4}$$

$$Z = \frac{S^2}{\rho\kappa} \tag{5}$$

C. *Making Thermoelectric Generator*

A thermoelectric generator composed of ten bulks, copper (Cu) electrodes, and mica sheets as shown in Fig. 6. Each bulk of 0.30 cm width, 0.40 cm length, and 2.00 cm height were used and connected in series by Cu wires and sheets (0.30 cm width, 0.80 cm length, and 0.05 cm thickness). Two mica sheets (2.00 cm width, 4.00 cm length, and 0.20 cm thickness) are used for the thermal translation from the hot and cold plates. The open circuit voltage (V_O) and internal resistance (R_I) were measured.

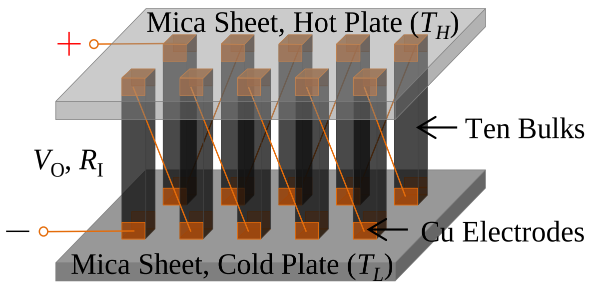

Figure 6. Making thermoelectric generator

III. Results and Discussion

A. Preparation and Characterizations of Samples

X-ray fluorescence (XRF) was used for the analysis of chemical composition. The concentrations of compounds are given in Table I. From this table found that a mineral specimen included the maganese oxide (MnO) 54.81%, iron (III) oxide (Fe_2O_3) 21.69%, silicon dioxide (SiO_2) 7.86%, barium oxide (BaO) 7.25%, aluminium oxide (Al_2O_3) 5.40% and others. Phase identifications were analyzed using X-ray diffraction (XRD) 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) such as MnO (04-0326), Fe_2O_3 (89-8104), SiO_2 (89-7499), BaO (74-1228) and Al_2O_3 (89-3072) were detected. XRF and XRD results indicated that a mineral sample comprised the MnO-Fe_2O_3-SiO_2-BaO-Al_2O_3-others.

TABLE I. Chemical Composition of Local Mineral

Compounds	Concentrations (%)
Maganese oxide (MnO)	54.81
Iron (III) oxide or Feric oxide (Fe_2O_3)	21.69
Silicon dioxide (SiO_2)	7.86
Barium oxide (BaO)	7.25
Aluminium oxide (Al_2O_3)	5.40
Potassium oxide (K_2O)	0.89
Magnesium oxide (MgO)	0.49
Calcium oxide (CaO)	0.41
Titanium dioxide (TiO_2)	0.30
Nickel oxide (NiO)	0.23
Copper oxide (CuO)	0.17
Cobalt oxide (Co_3O_4)	0.15
Strontium oxide (SrO)	0.10
Zinc oxide (ZnO)	0.07
Sodium oxide (Na_2O)	0.06
Phosphorus pentoxide (P_2O_5)	0.06
Yttrium oxide (Y_2O_3)	0.02
Sulphur trioxide (SO_3)	0.01
Arsenic trioxide (As_2O_3)	0.01

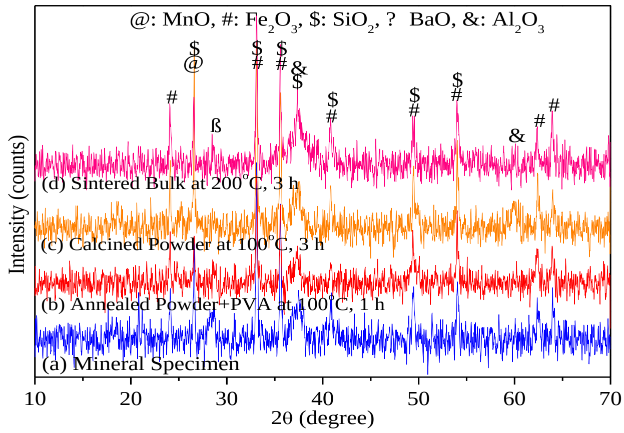

Figure 7. XRD patterns of mineral samples

B. Thermoelectric Properties and Efficiencies

Determination results of the thermoelectric properties and efficiencies at room temperature in air of the local mineral (MnO-Fe_2O_3-SiO_2-BaO-Al_2O_3-others) such as the type of charge carrier, Seebeck coefficient, electrical resistivity, thermal conductivity, power factor and figure of merit are presented and discussed.

Hot probe experiment exhibited that a bulk sample showed n-type material. The thermoelectric voltage (ΔV) decreased with increasing temperature difference (ΔT) from $\Delta V = -5.10$ V at $\Delta T = 5.40$ K to $\Delta V = -30.10$ V at $\Delta T = 78.40$ K, as shown in Fig. 8. Seebeck coefficients (S) of –0.94 mV/K to –0.38 mV/K are obtained.

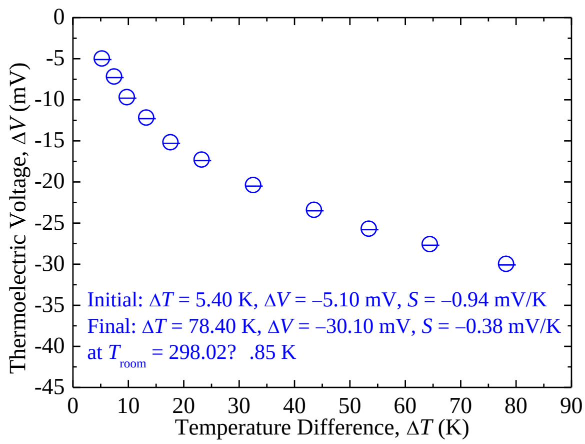

Figure 8. Thermoelectric voltage as a function of temperature difference

Measuring electrical characteristics indicated that the electrical resistivity (ρ) decreased with increasing current (I) and voltage (V) from ρ = 1.38 kΩ·m, I = 0.1 mA and V = 31 V to ρ = 1.08 kΩ·m, I = 1.2 mA and V = 290 V, as shown in Fig. 9.

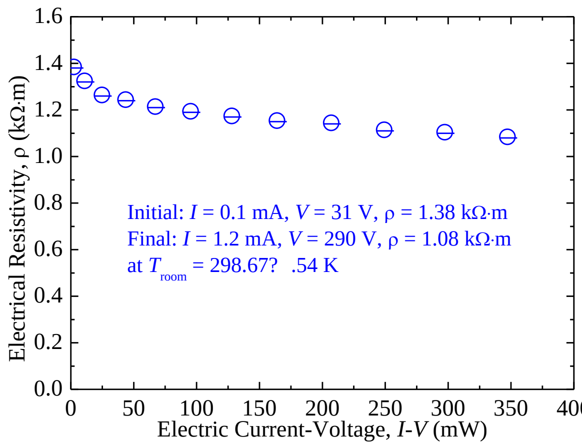

Figure 9. Resistivity as a function of current-voltage

Steady state technique showed that the thermal conductivity (κ) increased with increasing heat flux density (Φ_Q) from κ = 228.64 W/m·K and Φ_Q = 22.86 kW/m^2 to κ = 505.49 W/m·K and Φ_Q = 379.12 kW/m^2, as shown in Fig. 10.

Calculation results gave the values of P and Z were about 10^{-9} W/m·K^2 and 10^{-11} K^{-1}, respectively.

C. *Test on Thermoelectric Generator and Results*

A thermoelectric generator of MnO-Fe_2O_3-SiO_2-BaO-Al_2O_3-others is shown in Fig. 11. For preliminary test, a built generator was used to generate the electricity. A hot plate (absorbed heat, T_H) was placed on a generator to heat at 312-427 K. A cold plate (released heat, T_L) was surrounded by air at room temperature. The temperature difference ($\Delta T = T_H - T_L$), open circuit voltage (V_O), and internal resistance (R_I) were measured. Test results found that the open circuit voltage increased with increasing temperature difference from V_O = 9.3 mV at ΔT = 9 K (T_H = 312 K and T_L = 303 K) up to V_O = 66.0 mV at ΔT = 88 K (T_H = 427 K and T_L = 339 K). While the internal resistance decreased from 14.9 MΩ to 4.5 MΩ.

IV. CONCLUSIONS

A thermoelectric generator was made using ten bulks of a local mineral (MnO-Fe_2O_3-SiO_2-BaO-Al_2O_3-others), which has been found at Loei Province, Thailand. A bulk sample showed n-type material. The Seebeck coefficient, electrical resistivity, and thermal conductivity were about -10^{-3} V/K, 10^3 Ω·m, and 10^2 W/m·K, respectively. The power factor of ~10^{-9} W/m·K^2 and figure of merit of ~10^{-11} K^{-1} were obtained. Preliminary test demonstrated that a built generator can be generated the electricity. The open circuit voltage increased with increasing temperature difference from 9.3 mV at 9 K up to 66.0 mV at 88 K. Therefore, it can be used as an important platform for further research and development of thermoelectric technology.

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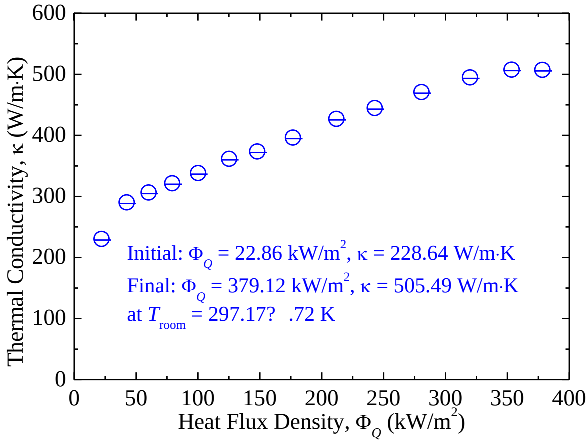

Figure 10. Thermal conductivity as a function of heat flux

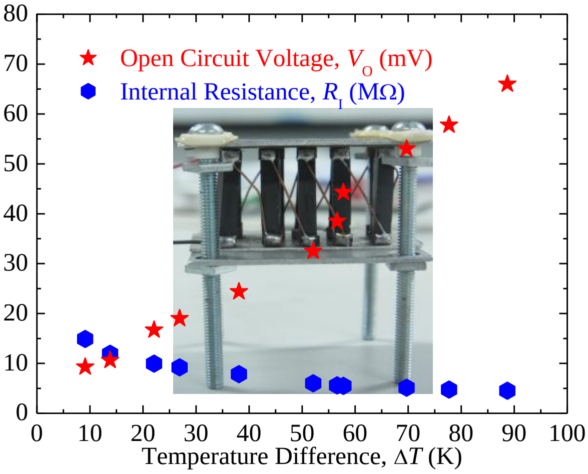

Figure 11. Test on a thermoelectric generator and results

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