P-$Ca_3Co_4O_9$ DOPED Ag AND N-$Ca_{0.97}Bi_{0.03}MnO_3$ MATERIALS FOR THERMOELECTRIC REFRIGERATOR

Supasit Paengson[1], Kunchit Singsoog[1,2], Panida Pilasuta[1], Wanatchaporn Namhongsa[1], and Tosawat Seetawan[1,2*]

[1]*Program of Physics, Faculty of Science and Technology, Sakon Nakhon Rajabhat University, Sakon Nakhon, 47000, Thailand*
[2]*Thermoelectrics Research Center, Research and Development Institution, Sakon Nakhon Rajabhat University, Sakon Nakhon, 47000, Thailand*

Received 22 December 2014; Revised 15 April 2015; Accepted 15 April 2015

ABSTRACT

Generally, the thermoelectric refrigerator fabricated form semimetal such as Bi_2Te_3, PbTe, and SiGe which high performance materials but a semimetal has toxic, expensive, and sensitive electrical shock. In this work, the possibility using oxide materials for fabricated thermoelectric refrigerator. The oxide thermoelectric refrigerator was fabricated from P-$Ca_3Co_4O_9$ doped Ag and N-$Ca_{0.97}Bi_{0.03}MnO_3$ materials. These materials were synthesized by solid state reaction method. The fabrication using melting method for connected materials with aluminum electrode. The thermoelectric properties were measured by steady state method for evaluated dimensionless figure of merit (ZT) and coefficient of performance (COP).

KEYWORDS: *oxide thermoelectric refrigerator, P-$Ca_3Co_4O_9$ doped Ag, N-$Ca_{0.97}Bi_{0.03}MnO_3$, coefficient of performance*

* Corresponding authors; e-mail: t_seetawan@snru.ac.th, Tel.&Fax +6642744319

INTRODUCTION

The thermoelectric refrigerator or thermoelectric cooler are used Peltier effect for change electrical power to temperature gradient [1]. Normally thermoelectric materials for fabrication thermoelectric refrigerator used semimetal such as Bi_2Te_3, PbTe, and SiGe (ZT ≈ 0.3-0.17) [2, 3] which high performance and good thermoelectric properties. The performance of thermoelectric materials is determined by dimensionless figure of merit (ZT) [1].

$$ZT = \frac{S^2 T}{\rho \kappa} \quad (1)$$

where S, ρ, κ and T is Seebeck coefficient, electrical resistivity, thermal conductivity and absolute temperature respectively. The coefficient of performance (COP) for refrigerator has directly related to ZT value [1,4].

$$COP_{\max} = \frac{T_c}{T_h - T_c} \bullet \frac{(\sqrt{1+ZT_{\mathrm{m}}} - \frac{T_h}{T_c})}{(\sqrt{1+ZT_{\mathrm{m}}} + 1)} \quad (2)$$

where T_c and T_h are cold side and hot side temperature of thermoelectric materials respectively, and ZT_{m} is figure-of-merit at average temperature of T_c and T_c. The fabrications of thermoelectric refrigerator are connecting materials series, but are thermal parallel.

Major development of oxide thermoelectric materials concentrated to fabrication generator but using oxide materials for refrigerator so few. The aims of this research are measured thermoelectric properties, dimensionless figure of merit and coefficient of performance oxide refrigerator fabricated from P-$Ca_3Co_4O_9$ doped Ag and N-$Ca_{0.97}Bi_{0.03}MnO_3$

MATERIALS AND METHODS

1) Synthesis and Fabrication

The P-$Ca_3Co_4O_9$ doped Ag and N-$Ca_{0.97}Bi_{0.03}MnO_3$ bulks prepared form powder P-$Ca_3Co_4O_9$ doped Ag and N- $Ca_{0.97}Bi_{0.03}MnO_3$ which synthesized by solid state reaction method or SSR method. Firstly we using calcium carbonate powder ($CaCO_3$ 100.09 g/mol, purity~ 99%, Sigma-Aldrich Co.) were mixed with cobalt oxide powder (Co_2O_3 165.86 g/mol, purity ~ 99.9%, Sigma-Aldrich Co.) and silver (Ag 87 g/mol, purity~ 99.9%). The N-type used calcium carbonate powder mixed with manganese dioxide (MnO_2 86.94 g/mol, purity 99.9%, Ajax Finechem Pty Ltd.) and bismuth oxide (Bi_2O_3 465.96 g/mol purity 99.9%, Sigma-Aldrich Co) purity in molar ratios. The mixed $CaCO_3$+Co_2O_3+Ag for P-$Ca_3Co_4O_9$ doped Ag and mixed $CaCO_3$+ MnO_2+Bi_2O_3 for N-$Ca_{0.97}Bi_{0.03}MnO_3$ were calcined at 1123 K for 10 h and 1323 K for 24 h in air, respectively. The calcined P-type powder was pressured of 21.57 MPa due to bulks sintered at 1223 K for 12 h. The calcined N-type powder was pressured of 9.80 MPa for bulks sintered at 1423 K for 36 h in air, respectively. Subsequently, the sintered bulks were cutting and polishing using the precision saw and grinder polisher (Isomet Low Speed Saw and WaterServ 3000 Ltd, USA) to obtain the legs shape of the thermoelectric cell. Confirm powder by x-ray diffraction (XRD) patterns have been performed on XRD-6100 SHIMADZU real time multiple strip detector, using Cu-Kα radiation and operating at 2 kW room temperature. The scans have been recorded from 10° to 80° (2θ). Thermoelectric properties Seebeck coefficient, electrical resistivity and thermal conductivity of the bulks sintered measurement by steady state ranging around 303K to 473K. Thermoelectric refrigerator cell was fabricated from P-N legs size of 2.5×2.5×10 mm^3 prior connect P-N junction must solder Pb on top and bottom legs for could connect with aluminum electrode. The total resistant of thermoelectric refrigerator cell is ≈ 2.5 Ω. How to select P and N legs for fabricated thermoelectric refrigerator cell are selected from synthesis condition has lowest total resistant of P-$Ca_3Co_4O_9$ doped Ag and N-$Ca_{0.97}Bi_{0.03}MnO_3$ bulks.

2) Measurement coefficient of performance

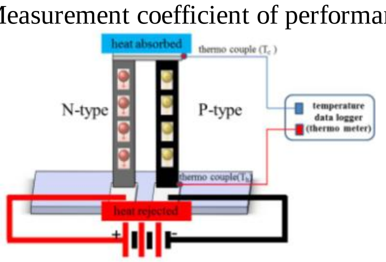


Fig. 1. modeling measurement of thermoelectric refrigerator cell

Fig.1 shown modeling measurement system of thermoelectric refrigerator cell. The red wire from refrigerator cell connected with the positive power supply and the black wire connected with negative power supply measured compared heat adsorbed (cold side) and heat rejected hot side temperature by thermocouple K-type. [5]

RESULTS AND DISCUSSION

Thermoelectric properties

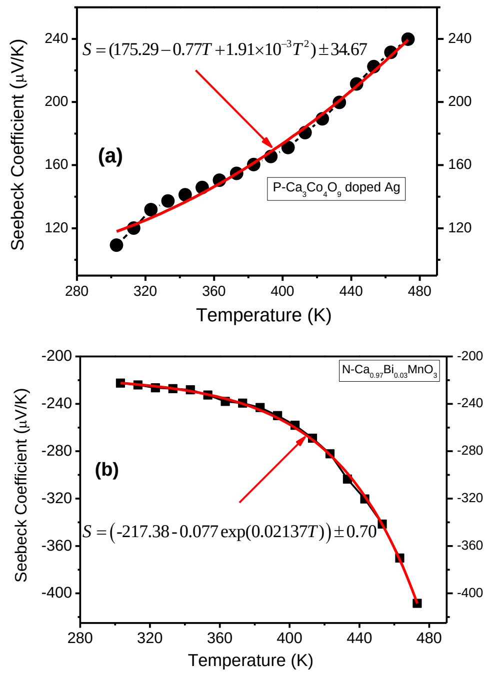
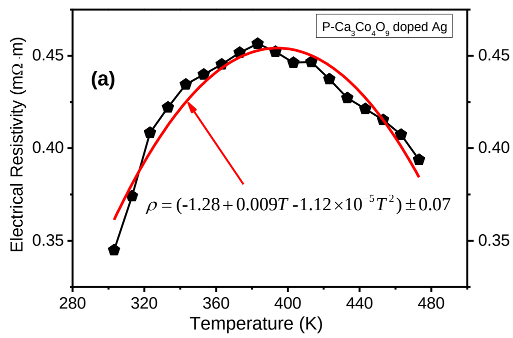


Fig. 2. Temperature dependence of the Seebeck coefficient for bulks P-$Ca_3Co_4O_9$ doped Ag and N-$Ca_{0.97}Bi_{0.03}MnO_3$

The relationship of Seebeck coefficient and temperature of P-$Ca_3Co_4O_9$ doped Ag at 303-473 K as shown Fig.2 (a). The Seebeck coefficient of P-$Ca_3Co_4O_9$ doped Ag values were linearly increased with increasing temperature. The relationship of Seebeck coefficient and temperature of $Ca_{0.97}Bi_{0.03}MnO_3$ at 303-473 K as shown Fig.2 (b). The Seebeck coefficient of $Ca_{0.97}Bi_{0.03}MnO_3$ values were exponentially increased with increasing temperature.



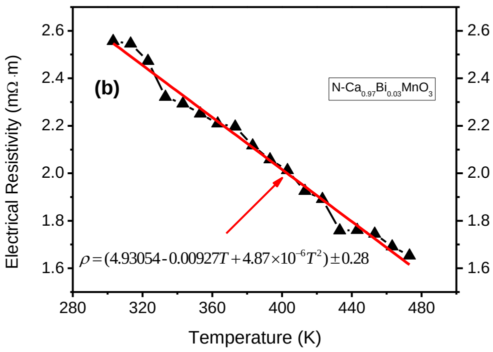


Fig. 3. Temperature dependence of the electrical resistivity for P-$Ca_3Co_4O_9$ doped Ag and N-$Ca_{0.97}Bi_{0.03}MnO_3$

Electrical resistivity of P-$Ca_3Co_4O_9$ doped Ag was depended temperature at 303-473 K as shown in Fig.3 (a). The electrical resistivity slowly fluctuation because P-$Ca_3Co_4O_9$ doped Ag was mixed phase. Electrical resistivity of N-$Ca_{0.97}Bi_{0.03}MnO_3$ was depended temperature at 303-473 K as shown in Fig.3 (b). The Seebeck coefficient of $Ca_{0.97}Bi_{0.03}MnO_3$ values were linearly decreased with increasing temperature.

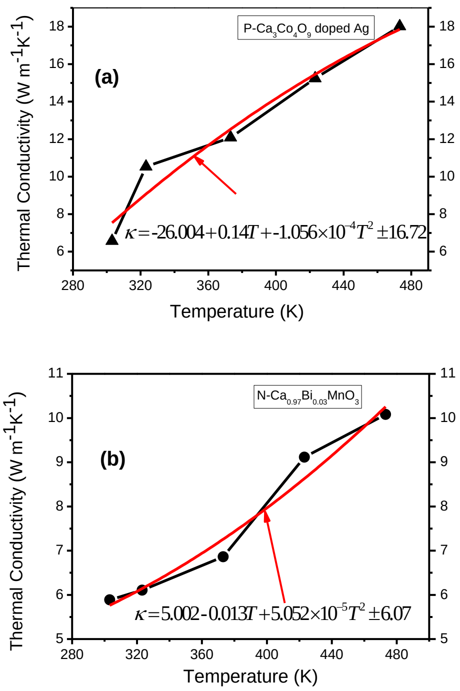


Fig. 4. Temperature dependence of the thermal conductivity for P-$Ca_3Co_4O_9$ doped Ag and N-$Ca_{0.97}Bi_{0.03}MnO_3$

Thermal conductivity of P-$Ca_3Co_4O_9$ doped Ag and N-$Ca_{0.97}Bi_{0.03}MnO_3$ as shown Fig.4 (a) and (b) respectively. The thermal conductivity of P-$Ca_3Co_4O_9$ doped Ag and N-$Ca_{0.97}Bi_{0.03}MnO_3$ were linearly increased with the increasing of temperature.

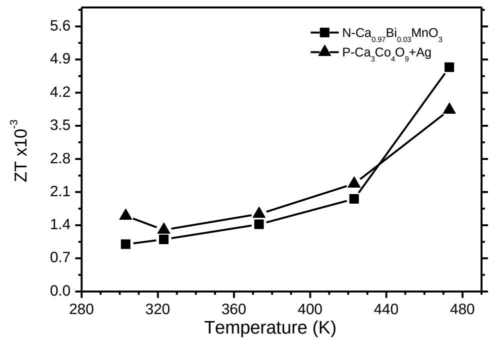


Fig. 5. Temperature dependence of the dimensionless figure of merit for bulks P-$Ca_3Co_4O_9$ doped Ag and N-$Ca_{0.97}Bi_{0.03}MnO_3$

The temperature dependent of the dimensionless figure of merit for P-$Ca_3Co_4O_9$ doped Ag and N-$Ca_{0.97}Bi_{0.03}MnO_3$ has a maximum value at 473 K which evaluated from equation (1) ZT≈ 0.0038 and 0.0047 respectively.

Temperature decrease triggered by current

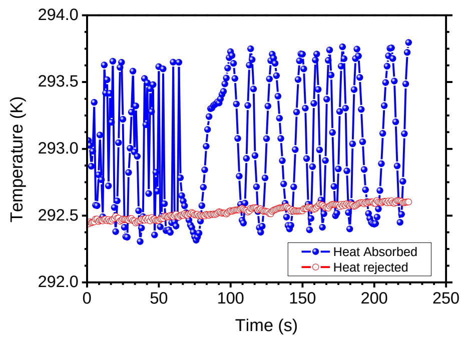


Fig. 6. Example Peltier effect relation between heats absorbed (cold side) heats rejected (hot side) when used electrical current 0.04 A voltage 0.1 V

When give electrical current to thermoelectric refrigerator cell a heats absorbed (cold side) temperature decreased nearly to heats rejected (hot side) and next time decreasing lowest temperature in heats rejected (hot side) .The next a temperature increased because heats rejected (hot side) can't rejected heat from cell not enough and successive. The coefficient of performance (COP) evaluated by equation (2)

The relationship of coefficient of performance and electrical current at 20-180 mA as shown Fig.7. Coefficient of performance value at 20-160 mA increased with increasing electrical current but in 180 mA sharply decreased because oxide thermoelectric refrigerator cell can't reject heat from cell not enough and successive influence to decreased cooling in cold side.

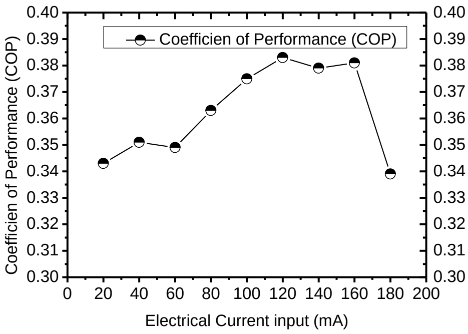


Fig. 7. Coefficient of performance (COP) of oxide thermoelectric refrigerator

CONCLUSION

P-$Ca_3Co_4O_9$ doped Ag and N-$Ca_{0.97}Bi_{0.03}MnO_3$ were synthesized using solid state reaction method and P-type and N-type materials shown crystal structure are orthorhombic. The thermoelectric properties were Seebeck coefficient and electrical resistivity shown good thermoelectric properties. The thermal conductivity is increased because has doping metal in structure of materials which have effect to dimensionless figure of merit (ZT) low value. The coefficient of performance very low because of Z lowed. However we find a Peltier effect in oxide refrigerator has COP ≈ 0.36

ACKNOWLEDGEMENTS

This research has financially supported by Thermoelectrics Research Center and Research and Researcher for Industry (RRi).

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