Thermoelectric properties of $Ca_3Co_4O_9$-$Bi_{0.5}Na_{0.5}TiO_3$ and Na_xCoO_2-$Bi_{0.5}Na_{0.5}TiO_3$ ceramics fabricated by spark plasma sintering

P-type layered cobalt oxides, Na_xCoO_2 (NCO) and $Ca_3Co_4O_9$ (CCO), are currently the two most investigated compounds with highest thermoelectric conversion performance for high-temperature energy harvesting applications[1,2,3]. Above 700 K, the ZT values for NCO and CCO can reach the value of about 0.8 – 1.0[3,4]. However, it is practical to investigate these compounds in order to improve their performances at lower temperature range for the purpose of replacing the current non-oxide compounds used in thermoelectric devices. The advantages of these compounds include the ease of fabrication and stability against oxidation environment. By employing cationic and anionic substitution using $Bi_{0.5}Na_{0.5}TiO_3$ (BNT), we hope to obtain a systematic favorable change in thermoelectric properties of these compounds.

In this study, a varying amount up to 0.07 mol fraction of BNT powder was doped in CCO and NCO powders by mechanical mixing in ethanol. Ceramics were fabricated by spark plasma sintering (SPS) the CCO-*x*BNT and NCO-*x*BNT mixtures at 900 °C (5 min) and 850 °C (3 min), respectively, under the pressure of 100 MPa in vacuum.

For CCO-*x*BNT ceramics, it was found that small addition of up to 0.03BNT caused a decrease in electrical conductivity while the Seebeck coefficient increased. With higher doping concentration, the opposite effects occurred. Since the thermal conductivity was lower only when 0.01BNT was added to CCO, the maximum value of ZT was obtained for CCO-0.01BNT ceramic as shown in Fig. 1. Due to the increasing trend of Seebeck coefficient with increasing temperature, this resulted in the larger ZT values at higher temperature. Overall, the thermoelectric performance of CCO-xBNT ceramics was virtually independent of BNT concentration.

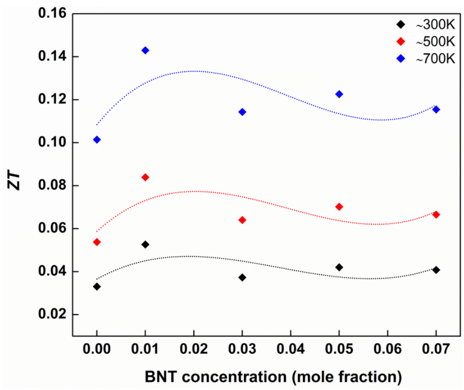

Fig. 1. The variation of ZT values of CCO-xBNT ceramics with BNT content at various temperatures.

The ZT values for NCO-xBNT ceramics are shown in Fig. 2. In contrast to the CCO-xBNT system, the addition of BNT caused the thermoelectric performance to decrease. This was mainly due to a large reduction of the electrical conductivity by nearly one order of magnitude while Seebeck coefficient remained about the same values regardless of added BNT content. The thermal conductivity was reduced only at small doping concentration.

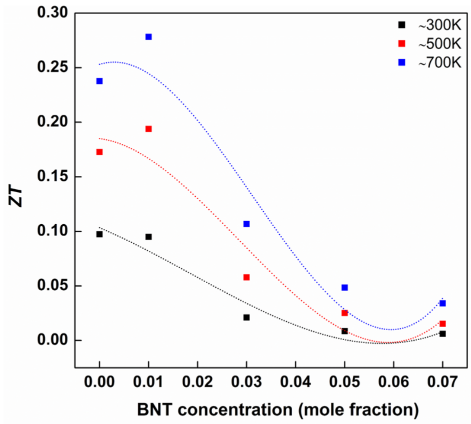

Fig. 2. The variation of ZT values of NCO-xBNT ceramics with BNT content at various temperatures.

From this investigation, a small BNT addition (≤ 0.03 mol fraction) could result in a slight increase in thermoelectric performance in both CCO and NCO compounds while no advantage was gained with addition of higher BNT content.

Keywords: ceramic, oxide, thermoelectric
Full Name: Anucha Watcharapasorn, Department of Physics and Materials Science, Chiang Mai University, Thailand
E-mail: anucha@stanfordalumni.org

References

[1] I. Terasaki, Physica., 2003, B328:63-67.
[2] P.H. Xiang, Y. Kinemuchi, H. Kaga, K. Watari, J. Alloy. Compd., 2008, 454:364-369.
[3] N. Li, Y. Jing, G. Li, C. Wang, J. Shi, D. Yu, J. Alloy. Compd., 2009, 467:444-449.
[4] D. Wang, L. Cheng, Q. Yao, J. Li, Solid. State. Commun., 2004, 129:615-618.