

# Synthesis and Thermoelectric Properties of Misfit Cobaltites, $[\text{Bi}_{2-\delta}\text{Sr}_{2-x}\text{Co}_x\text{O}_4]_{\text{RS}}[\text{CoO}_2]_{\text{p}}$

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Two single phase Bi-Sr-based misfit cobaltites, built up from the stacking of rock-salt-type (RS) layers and hexagonal  $[\text{CoO}_2]$  layers (H), have been synthesized by standard solid state reaction. The average composition of these samples are close to Bi:Sr:Co=2:1.9:2.1 and Bi:Sr:Co:=2:2.1:2.4. Previously, the value of p was 1.8, but in the present study it seems to be  $\sim 1.91$ , that is the highest among those of the similar incommensurate misfit cobalt oxides reported so far. The chemical formula of the obtained cobaltites can be expressed as  $[\text{Bi}_{2-\delta}\text{Sr}_{2-x}\text{Co}_x\text{O}_4]_{\text{RS}}[\text{CoO}_2]_{\text{p}=1.91}$  for these samples based on their p value. Electrical resistivity of both samples exhibit metallic behavior in the temperature range from 350 K to 1073 K. Seebeck coefficient increases with increasing temperature and at it reaches up to about  $165 \mu\text{V K}^{-1}$  for the sample with composition Bi:Sr:Co=2:1.9:2.1 and  $172 \mu\text{V K}^{-1}$  for the sample with composition Bi:Sr:Co=2:2.1:2.4 at 1000 K. The highest power factor of  $1.3 \times 10^{-4} \text{ W/mK}^2$  is obtained for the latter sample resulting from its lower resistivity and higher Seebeck coefficient than that observed for the former sample (of  $1.1 \times 10^{-4} \text{ W/mK}^2$ ).

Keywords: thermoelectric compound, misfit-layered cobaltite, Seebeck coefficient, thermopower,

## 1. INTRODUCTION

The extensive studies on thermoelectric (TE) oxide materials are accelerated by the discovery of high figure of merit  $Z$  (where  $Z=S^2/\rho\kappa$ , where  $S$ ,  $\rho$  and  $\kappa$  are for Seebeck coefficient, resistivity and thermal conductivity, respectively) in  $\text{NaCo}_2\text{O}_4$  single crystal [1]. The structure of misfit-layered cobaltites also consist of similar  $\text{CdI}_2$ -type  $\text{CoO}_2$  layers and block layers, being similar to the  $\text{NaCo}_2\text{O}_4$  [2]. They are stacked with the rock-salt (RS)-type separating block layers [3-5]. The misfit character reflects the incommensurability of the  $\text{CdI}_2$ -type and block layers parallel to the b-axes, namely  $b_{\text{H}}$  and  $b_{\text{RS}}$  axes, but the a and c axes are in common [4, 5]. All the misfit-layered cobaltites (e.g.,  $[\text{Ti}_{0.8}\text{Co}_{0.2}\text{Sr}_2\text{O}_3]_{\text{RS}}[\text{CoO}_2]_{\text{p}=1.8}$ ,  $[\text{Ca}_2\text{CoO}_3]_{\text{RS}}[\text{CoO}_2]_{\text{p}=1.62}$ , and  $([\text{Bi}_{0.87}\text{SrO}_2]_2\text{RS} [\text{CoO}_2]_{\text{p}=1.82}$  etc.) [3-6] have the incommensurate character of the modulation with  $p$  ( $=b_{\text{RS}}/b_{\text{H}}$ ) = 1.62  $\sim$  1.82 except for  $[\text{Bi}_2\text{Ba}_{1.8}\text{Co}_{0.2}\text{O}_4]_{\text{RS}}[\text{CoO}_2]_{\text{p}=2}$  with  $p=2$  that has been reported recently [8]. All these incommensurate misfit cobaltites show rather similar thermopower (TEP) values to that of  $\text{NaCo}_2\text{O}_4$  [5, 6, and 7]. Surprisingly, Sr-rich (Co-poor) region has been investigated so far in the Bi-system [9, 10]. The systematic studies around Bi:Sr:Co:=2:2:2 region had never been done for Bi-Sr-based misfit cobaltites. In the present article, we report on the investigation and synthesis of single phase samples of Bi-Sr based misfit layered cobaltites in the vicinity of Co-rich region and present their

thermoelectric properties.

## 2. EXPERIMENTAL

The polycrystalline samples of Bi-Sr-based misfit cobalt oxides were prepared by the standard solid-state reaction method. Appropriate amounts of  $\text{SrCO}_3$  (99.99 %),  $\text{Bi}_2\text{O}_3$  (99.99 %) and  $\text{Co}_3\text{O}_4$  (99.99 %) powders were mixed in an agate mortar and pressed into pellets. The pellets were heated at 1073 K for 12 h in air. Then, the samples were furnace-cooled to room temperature. After grinding, the powders were re-pelletized and heated at 1123 K for 12 h in air followed by the furnace-cooling. The structure and phase purity of prepared samples were checked by powder X-ray diffraction (XRD) at room temperature by a two-axis diffractometer (Rigaku Co. with  $\text{CuK}\alpha$  radiation,  $\lambda=1.54 \text{ \AA}$ ) equipped with a curved-graphite monochromator. The electrical resistivity and the Seebeck coefficient were measured in the temperature range from 353 K to 1023 K using an automated Seebeck coefficient measuring apparatus, Ozawa RZ2001i. The thermal conductivity measurement was performed using a steady-state heat-flux measurement apparatus, ULVAC GH-1S in the temperature range from 300 K to 600 K.

## 3. RESULTS AND DISCUSSION

Fig. 1 shows a triangular phase diagram of  $1/2 \text{ Bi}_2\text{O}_3$



resistivity for both samples are comparable with that of previously reported polycrystalline sample of the BC-222 system [10]. The Seebeck coefficient increases with increasing temperature for both samples. At 300 K, the Seebeck coefficient for both samples are almost the same, i.e., about 110  $\mu\text{V/K}$ , but at 1000 K it becomes about 170  $\mu\text{V/K}$  for the sample B and 165  $\mu\text{V/K}$  for the sample A. The power factors of both samples are plotted in Fig. 5. The maximum power factor,  $S^2/\rho$  ( $\text{W/mK}^2$ ) =  $1.3 \times 10^{-4}$  was observed for the sample B and a little

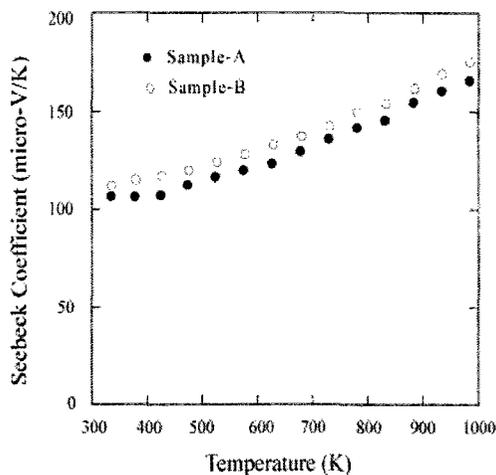


Fig.4. Seebeck co-efficient vs. temperature of samples A and B.

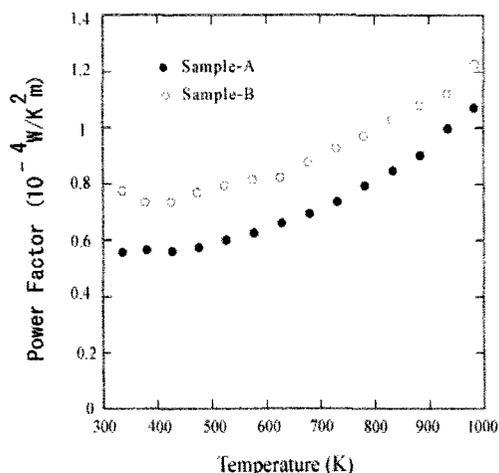


Fig.5. Power factor vs. temperature of samples A and B.

lower power factor of  $1.1 \times 10^{-4} \text{ W/mK}^2$  was observed for the sample A, at 1000 K.

Between 300 K and 600 K, the thermal conductivity was measured for the sample A. The room temperature  $\kappa$  values is 0.7  $\text{W/mK}$ . The magnitude of  $\kappa$  for this sample is almost linear over the measured temperature range and reaches up to about 0.9  $\text{W/mK}$  at 600 K. This low  $\kappa$  could be due to the incommensurated crystallographic structure. Using  $\rho$ ,  $S$ , and  $\kappa$  values, we can evaluate the thermoelectric Figure-of-merit,  $Z$  ( $S^2/\rho\kappa$ ) =  $1.3 \times 10^{-4} \text{ K}^{-1}$  for the sample A and  $1.1 \times 10^{-4} \text{ K}^{-1}$  for the sample B using the same  $\kappa$  value. The dimensionless

figure-of-merit  $ZT$  at 300 K is then 0.033 for the sample A (Bi:Sr:Co=2:1.9:2.1) and 0.040 for the sample B (Bi:Sr:Co=2:2.1:2.4). The  $ZT$  values for the present two samples at 300 K are approximately equal to the polycrystalline sample of  $\gamma\text{-Na}_{0.70}\text{CoO}_2$  [11] and  $[\text{Ca}_2\text{CoO}_3]_{0.62}\text{CoO}_2$  [12]; indicating that the present samples would be potential candidate for a TE material. It is seen from the present studies that the TE properties are relatively better for the sample B than that of the sample A.

#### 4. CONCLUSION

Two Bi-Sr-based misfit layered cobalt oxides with composition close to Bi:Sr:Co=2:1.9:2.1 and Bi:Sr:Co=2:2.1:2.4 have been synthesized successfully for which we proposed a common chemical formula  $[\text{Bi}_{2-x}\text{Sr}_x\text{Co}_x\text{O}_4]_{\text{RS}}[\text{CoO}_2]_{\text{p}=1.91}$  based on the b axis ratio  $p$  of the two subsystems. The  $p$  value obtained for both systems seem to be the highest among other incommensurate misfit cobaltites of composite structure. Among the TE properties,  $\rho$  values are relatively higher for the present compounds and it must be lowered for the practical application.

#### REFERENCES

- [1] I. Terasaki, Y. Sasago, and K. Uchinokura, *Phys. Rev. B* **56**, 12685 (1997).
- [2] D. J. Singh, *Phys. Rev. B* **61**, 13397 (2000).
- [3] Ph. Boullay, B. Domenges, H. Hervieu, D. Groult, and B. Raveau, *Chem. Mater.* **8**, 1482 (1996).
- [4] H. Leligny, D. Grebille, O. Perez, A.C. Masset, M. Hervieu, C. Michel and B. Raveau, *C.R. Acad. Sci., Ser. IIc: Chim* **2**, 409 (1999).
- [5] A.C. Masset, C. Michel, A. Maignan, M. Hervieu, O. Toulemonde, F. Studer, B. Raveau, and J. Hejtmanek, *Phys. Rev. B* **62**, 166 (2000).
- [6] A. Maibnan, L.B. Wang, S. Hebert, D. Pelloquin, and B. Raveau, *Chem. Mater.* **14**, 1231 (2002).
- [7] T. Itoh and I. Terasaki, *Jpn. J. Appl. Phys. Part 1* **39**, 6658 (2000).
- [8] M. Hervieu, A. Maignan, C. Michel, V. hardy, N. Creon, and B. raveau, *Phys. Rev. B* **67**, 045112-1 (2003).
- [9] H. Leligny, D. Grebille, O. Perez, A.C. Masset, M. Hervieu, B. Raveau, *Acta Crystall. B* **56**, 173 (2000).
- [10] G. Xu, R. Funahashi, M. Shikano, I. Matsubara and Y. Zhou; *J. Appl. Phys.* **91**, 4344 (2002).
- [11] Y. Ono, R. Ishikawa, Y. Miyazaki, and T. Kajitani, *J. Phys. Soc. Jpn.* **70**, (Suppl. A) 235 (2001).
- [12] Y. Miyazaki, Y. Suzuki, M. Onoda, Y. Ishii, Y. Morii and T. Kajitani, *Jpn. J. Appl. Phys.* **43**, 9A 6252 (2004).

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