Synthesis and Thermoelectric Properties of Misfit Cobaltites, [Bi_{2-δ}Sr_{2-x}Co_xO₄]_{RS}[CoO₂]_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 [CoO₂] 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 ~ 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 $[Bi_{2-\delta}Sr_{2-x}Co_xO_4]_{RS}[CoO_2]_{p=1.91}$ 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 μ V K⁻¹ for the sample with composition Bi:Sr:Co=2:1.9:2.1 and 172 μ V K⁻¹ for the sample with composition Bi:Sr:Co=2:1.9:2.1 and 172 μ V K⁻¹ for the sample with composition Bi:Sr:Co=2:1.9:2.1 and 172 μ V K⁻¹ for the sample with composition Bi:Sr:Co=2:1.9:2.1 and 172 μ V K⁻¹ for the sample with composition Bi:Sr:Co=2:1.9:2.1 and 172 μ V K⁻¹ for the sample with composition Bi:Sr:Co=2:1.9:2.1 and 172 μ V K⁻¹ for the sample with composition Bi:Sr:Co=2:1.9:2.1 and 172 μ V K⁻¹ for the sample with composition Bi:Sr:Co=2:1.9:2.1 and 172 μ V K⁻¹ for the sample with composition Bi:Sr:Co=2:1.9:2.1 and 172 μ V K⁻¹ for the sample with composition Bi:Sr:Co=2:1.9:2.1 and 172 μ V K⁻¹ for the sample with composition Bi:Sr:Co=2:1.9:2.1 and 172 μ V K⁻¹ for the sample with composition Bi:Sr:Co=2:1.9:2.1 and 172 μ V K⁻¹ for the sample with composition Bi:Sr:Co=2:2.1:2.4 at 1000 K. The highest power factor of 1.3×10⁻⁴ W/mK² is obtained for the latter sample resulting from its lower resistivity and higher Seebeck coefficient than that observed for the former sample (of 1.1×10⁻⁴ W/mK²).

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, ρ and κ are for Seebeck coefficient, resistivity and thermal conductivity, respectively) in NaCo₂O₄ single crystal [1]. The structure of misfit-layered cobaltites also consist of similar CdI₂-type CoO₂ layers and block layers, being similar to the NaCo₂O₄ [2]. They are stacked with the rock-salt (RS)-type separating block layers [3-5]. The misfit character reflects the incommensurability of the CdI₂-type and block layers parallel to the b-axes, namely b_{H} and b_{RS} axes, but the a and c axes are in common [4, 5]. All the misfit-layered cobaltites (e.g., $[TI_{0.8}Co_{0.2}Sr_2O_3]_{RS}[CoO_2]_{p=1.8}, [Ca_2CoO_3]_{RS}[CoO_2]_{p=1.62},$ and $([Bi_{0.87}SrO_2]_2RS [CoO_2]_{p=1.82}$ etc.) [3-6] have the incommensurate character of the modulation with p 1.62 for $(=b_{RS}/b_{H})=$ 1.82 except $[Bi_2Ba_{1,8}Co_{0,2}O_4]_{RS}[CoO_2]_{p=2}$ with p=2 that has been reported recently [8]. All these incommensurate misfit cobaltites show rather similar thermopower (TEP) values to that of NaCo₂O₄ [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 SrCO₃ (99.99 %), Bi₂O₃ (99.99 %) and Co₃O₄ (99.99 %) powders were mixed in an agate motor 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 diffractometer Co. with two-axis (Rigaku equipped λ=1.54 Å) with а CuKa radiation, monochromator. The electrical curved-graphite 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 ULVAC GH-1S in the measurement aparatus, temperature range from 300 K to 600 K.

3. RESULTS AND DISCUSSION

Fig. 1 shows a triangular phase diagram of 1/2 Bi₂O₃

- SrCO₃ (SrO) - 1/3 Co₃O₄ system indicating the investigated region. For comprehensive understanding, we expanded the region of the investigated area of the phase diagram as the right section in Fig. 1. Fig. 2 shows obtained powder XRD patterns of selected samples denoted by A, B, C, D and E. Closed circles indicate the impurity peaks and those peaks are assigned to Sr_{2.25}Bi_{6.75}O_{12.38}. It is clearly seen from Fig. 2 that the best sample, without any impurity, is obtained for the sample denoted by A and the sample denoted by B has one impurity peak; but we assumed it being close to the single phase range due to negligible impurity peak. The composition nominal of the sample Α is Bi:Sr:Co:=2:1.9:2.1 and that of B is Bi:Sr:Co:=2:2.1:2.4. For the sake of clarity, we shall keep using these notations of A and B for these two single phase Bi-Sr-based misfit cobaltites for the rest of this report.



Fig.1. Phase diagram of $1/2 \operatorname{Bi}_2O_3 - \operatorname{SrO}(\operatorname{SrCO}_3) - 1/3 \operatorname{Co}_3O_4$ at 840° C. Expanded region is shown in the right hand side of this figure.

The lattice parameters are calculated based on the d-values of XRD peaks using a standard least squares refinement method. The obtained lattice parameters are a=4.943 (8) Å, $b_{RS}=5.351$ (1) Å and c=29.96 (6) Å with β =93.5 (2)°. These values are approximately the same as those reported by Leligny et al. [4] for [Bi_{0.87}SrO₂]₂ $[CoO_2]_{p=1.82}$ (a=4.90 4 (1) Å, $b_{RS}=5.112$ (1) Å and c=29.864 (5) Å with β =93.49 (2)° for the subsystem 1 and $b_H=2.8081$ (5) Å for subsystem 2). For our convenience, we referred here the RS-type block layer (BL) for subsystem 1 and CoO₂ sheet for subsystem 2. It was difficult to determine the b_H length from the complex XRD pattern. It is reasonable to assume that the b-axis length of CoO₂ subsystem of this sample could also be the same as $b_{\rm H}=2.8081$ (5) Å reported for the sample in Ref. 9. When we put $b_{H}=2.8081$ (5) Å for our sample, the related misfit parameter is calculated to be $p = b_{RS}/b_{H}$ (5.35/2.8081)=1.91. To our knowledge, this value of p is the highest observed up to now for misfit layered cobaltites. By the same way, the obtained lattice parameters for the sample B, such as a=4.96 (2) Å, $b_{RS}=5.35$ (3) Å, c=30.1 (1) Å , $\beta=94.2$ (2)°. The p value becomes 1.91 taking $b_H=2.8081$ (5) Å from Ref. 9.

Now, two possible formulae of this new single phase cobaltites can be suggested on the basis of the b-axis ratio. Based on the nominal chemical ratio and the p-value, the chemical formula of the sample A becomes $[Bi_{2.6}Sr_{1.8}Co_{0.2}O_4]_{RS}[CoO_2]_{p=1.91}$, considering that Bi is slightly deficient, small amount of Co exists in the intermediate layers of the RS blocks. The chemical

formula of the sample B could be $[Bi_{2-\delta}Sr_{1.9}Co_{0.1}O_4]_{RS}[CoO_2]_{p=1.91}$. Some amounts of impurities such as $Sr_{2.25}Bi_{6.75}O_{12.38}$ and $SrCoO_x$ could exist in the sample A and B, respectively. In addition to the above discussion it should be pointed out here that it is far beyond the accuracy of the present technique to determine the exact oxygen content in the RS-type block and an accurate structure refinement must be undertaken by the X-ray single crystal and/or neutron powder diffraction.







Fig.3. Electrical resistivity vs. temperature of samples A and B.

The electrical resistivity, Seebeck coefficient and power factor were measured from 350 to 1073 K. Figures 4 and 5 show the electrical resistivity and Seebeck coefficient for the samples A and B. The electrical resistivity vs. temperature curves show that the present samples are metallic in the above temperature range. For the sample A, the electrical resistivity remains almost constant (20 m Ω cm, more or less) in the whole measured temperature range, whereas it is about 14 m Ω cm at 350 K but becomes about 20 m Ω cm at 1073 K for the sample B. These values of the electrical 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 μ V/K, but at 1000 K it becomes about 170 μ V/K for the sample B and 165 μ V/K for the sample A. The power factors of both samples are plotted in Fig. 5. The maximum power factor, S²/ ρ (W/mK²) = 1.3×10⁻⁴ 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 1.1×10^{-4} W/mK² 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 κ values is 0.7 W/mK. The magnitude of κ for this sample is almost linear over the measured temperature range and reaches up to about 0.9 W/mK at 600 K. This low κ could be due to the incommensurated crystallographic structure. Using ρ , S, and κ values, we can evaluate the thermoelectric Figure-of-merit, Z (S²/ $\rho\kappa$) = 1.3×10⁻⁴ K⁻¹ for the sample A and 1.1×10⁻⁴ K⁻¹ for the sample B using the same κ 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 γ -Na_{0.70}CoO₂ [11] and [Ca₂CoO₃]_{0.62}CoO₂ [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 $[Bi_{2-\delta}Sr_{2-x}Co_xO_4]_{RS}[CoO_2]_{p=1.91}$ 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, ρ 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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