Transport Properties in (Na, Ca)Co₂O₄ Ceramics

T. Itoh¹, T. Kawata¹, T. Kitajima¹ and I. Terasaki¹,²,*
¹Department of Applied Physics, Waseda University, Tokyo 169-8555, Japan
²Precursory Research for Embryonic Science and Technology, Japan Science Technology Corporation

Abstract

The resistivity and thermopower of polycrystalline NaₓCaₓCo₂O₄ were measured and analyzed. Both the quantities increase with x, suggesting that the carrier density is decreased by the substitutions of Ca²⁺ for Na⁺. Considering that the temperature dependence of the resistivity show a characteristic change with x, the conduction mechanism is unlikely to come from a simple electron-phonon scattering. As a reference for NaCo₂O₄, single crystals of a two-dimensional Co oxide Bi₂₋ₓPbₓMₓCo₂O₉ (M = Sr and Ba) were studied. The Pb substitution decreases the resistivity, leaving the thermopower nearly intact.

1 Introduction

A search for new thermoelectric (TE) materials is an old problem that has been reexamined to date [1]. Even though binary compounds might have been thoroughly studied, a thermoelectric material of higher performance might sleep in ternary, quaternary or more complicated compounds. A filled skutterudite is an example for newly discovered TE materials [2].

Very recently Terasaki, Sasago and Uchinokura have found that a layered Co oxide NaCo₂O₄, whose crystal structure is schematically drawn in Fig. 1, shows large thermopower (100 µV/K at 300 K) and low resistivity (200 µΩcm at 300 K) along the a axis [3]. A striking feature of this compound is that the thermopower of 100 µV/K is realized in the carrier density of 10²¹ cm⁻³. This is difficult to explain in the framework of the conventional band picture, and there should exist a mechanism to enhance the thermopower.

In conventional TE materials, the TE performance is optimized near a carrier density of 10¹⁹ cm⁻³. Thus we expect that the TE performance of NaCo₂O₄ may be improved by the reduction of the carrier density. The easiest way to change the carrier density is to substitute a divalent cation such as Ca²⁺ for a monovalent Na⁺. Motivated by this, we measured and analyzed the resistivity and thermopower of polycrystalline (Na, Ca)Co₂O₄. Another way is to study a two-dimensional Co oxide with low carrier density. For this purpose Bi₂Sr₃Co₂O₉ (The crystal structure is shown in Fig. 2) is most suitable, because the resistivity is lowered by the Ba-substitution for Sr [4] and the Pb substitution for Bi [5]. In addition, the optical reflectivity shows a small Drude weight [6]. We report on its transport properties in the latter part of the proceedings.

2 Experimental

Polycrystalline samples of NaₓCaₓCo₂O₄ were prepared in a conventional solid-state reaction [7]. An appropriate mixture of powdered NaCO₃, CaCO₃ and Co₃O₄ was calcined at 860°C for 12 h. The product was finely ground, pressed into a pellet, and sintered at 800°C for 6 h. The x-ray diffraction pattern showed no trace of impurities. Note that the a tiny trace of impurity phases was detected in the product from stoichiometric mixture (Na:Co=1:2), which indicates the evaporation of a small amount of Na. Thus we added excess Na of 10 at.% to prepare NaCo₂O₄.

Single crystals of Bi₂MₓCo₂O₉ (M = Sr and Ba) [8] and Bi₂₋ₓPbₓSr₃Co₂O₉ [9] were prepared by a self-flux technique. Crystals were platelike with typical dimensions of 1×1×0.01 mm³. As for the Pb substitution, we prepared two different crystals with nominal compositions of x=0.2 and 0.4.

Resistivity (ρ) was measured through a four-probe method. Thermopower (S) was measured with a nanovoltmeter (HP 34420A), where a typical resolution was 5–10 nV. Two edges of a sample was pasted on Cu sheets working as a heat bath, and the temperature gradient of
0.5–1 K was measured through a differential thermocouple made of copper-constantan. The contributions from copper leads were carefully subtracted.

3 Results and Discussion

Let us begin with the effect of excess Na on the resistivity of Na$_{1.1}$Co$_2$O$_4$. Na is an element difficult to control. First, it is quite volatile above 800°C. Secondly, residual Na is rarely observed in x-ray diffraction patterns, because it often exists as deliquesced NaOH in the grain boundary. Moreover the Na site in NaCo$_2$O$_4$ can change from 0 to 1. Figure 3 shows the temperature dependence of resistivity of polycrystalline samples of Na$_{1.1}$Co$_2$O$_4$. We attributed the increase of resistivity with Na to the excess Na in the grain boundaries, and regarded the sample for x = 0 as the parent material for Ca substitution.

Figures 4(a) and 4(b) show ρ and S of polycrystalline samples of Na$_{1.1}$Ca$_2$Co$_2$O$_4$. The magnitudes of resistivity and thermopower increase with x, suggesting that the carrier density is reduced by the Ca substitution. This is naturally understood from a viewpoint of Co valence. In NaCo$_2$O$_4$ the formal valence (p) of Co is 3.5+, i.e., Co$^{3+}$:Co$^{4+}$=1:1. The Ca substitution decreases p down to 3+, which corresponds to the configuration of (3d$^9$). Since the six electrons fully occupied the three dγ bands in the low spin state, oxides with Co$^{3+}$ are often insulating. As expected, the power factor $S^2/\rho$ is improved in x $\sim$0.15 by 20%. It should be emphasized that the Ca substitution changes the temperature dependence of resistivity. For example, while ρ for x=0 shows a positive curvature below 100 K, ρ for x=0.35 shows a negative curvature. This indicates that the scattering rate depends strongly on the carrier density, which is unlikely to arise from the electron-phonon scattering.

Next we discuss the thermoelectric properties of (Bi, Pb)$_2$M$\text{M}_2$Co$_2$O$_9$. In Figs. 5(a) and 5(b), ρ and S of Bi$_2$M$_2$Co$_2$O$_9$ single crystals along the in-plane direction are plotted as a function of temperature. ρ of the present samples reproduces the data in the literature, where the electric conduction for M=Ca is more metallic than that for M=Ba. Note that the magnitude of S is above 100 μV/K for both samples, owing to the small carrier density.

In contrast to the Ba substitution for Sr, Pb not only works as an acceptor, but also modifies the electronic states of Bi$_2$Sr$_2$Co$_2$O$_9$. Figures 6(a) and 6(b) show ρ and S of Bi$_2$Pb$_2$Sr$_2$Co$_2$O$_9$ single crystals along the in-plane direction. ρ is decreased drastically by the Pb substitution, which looks similar to Fig. 5(a). However, S remains nearly unchanged upon the Pb substitution, which clearly indicates that the Ba and Pb substitutions affect the electronic states differently. The anomalous electronic states of Bi$_2$Pb$_2$Sr$_2$Co$_2$O$_9$ are also suggested by the large negative magnetoresistance at low temperatures.

4 Summary

In summary, we prepared polycrystalline samples of Na$_{1.1}$Ca$_2$Co$_2$O$_4$ and single-crystal samples of Bi$_2$Pb$_2$Sr$_2$Co$_2$O$_9$ (M= Sr and Ba: x=0, 0.2 and 0.4). In Na$_{1.1}$Ca$_2$Co$_2$O$_4$, both the resistivity and the thermopower increase with x, which suggests that the carrier density is decreased by the Ca substitution. In Bi$_2$Pb$_2$Sr$_2$Co$_2$O$_9$, the resistivity is decreased by the Ba and Pb substitutions, but the doping effects on the thermopower are different. While the Ba substitution decreases the thermopower, the Pb substitution hardly changes the thermopower. This is a direct example that the resistivity can be lowered while the thermopower is kept large.

Acknowledgements

The authors would like to thank M. Takano, S. Nakamura, K. Fukuda, S. Kurihara and K. Kohn for fruitful discussions. They also appreciate H. Yakabe, K. Nakamura, K. Fujita and K. Kikuchi for collaboration. They are indebted to I. Tsukada for showing us the unpublished data of (Bi,Pb)$_2$Sr$_3$Co$_2$O$_9$. 

---

Fig. 3 Resistivity of polycrystalline samples of Na$_{1.1}$Co$_2$O$_4$.

![Graph showing Resistivity vs Temperature for Na$_{1.1}$Co$_2$O$_4$](image)

Fig. 4 (a) Resistivity and (b) thermopower of polycrystalline samples of Na$_{1.1}$Ca$_2$Co$_2$O$_4$.

![Graph showing Resistivity and Thermopower vs Temperature for Na$_{1.1}$Ca$_2$Co$_2$O$_4$](image)
References

[*] Corresponding author: Ichiro Terasaki
Phone and Fax: +81-3-5286-3854
E-mail: terra@mn.waseda.ac.jp.

[1] G. Mahan, B. Sales and J. Sharp, “Thermoelectric materials: New approaches to an old problem”, Physics Today, March, pp. 42-47 (1997).

[2] B. C. Sales, D. Mandrus, B. C. Chakoumakos, V. Keppens and J. R. Thompson, “Filled skutterudite antimonides: Electron crystals and phonon glasses”, Phys. Rev. B, Vol. 56, No. 23, pp. 15081-15089 (1997).

[3] I. Terasaki, Y. Sasago and K. Uchinokura, “Large thermoelectric power of NaCo$_2$O$_4$ single crystals”, Phys. Rev. B, Vol. 56, No. 20, pp. R12685-R12687 (1997).

[4] J. M. Tarascon, R. Ramesh, P. Barboux, M. S. Hedge, G. W. Hull, L. H. Green, M. Giroud, Y. LePage, W. R. McKinnon, J. V. Waszczak, and L. F. Schneemeyer, “New non-superconducting layered Bi-oxide phases of formula Bi$_2$M$_3$Co$_2$O$_9$ containing Co instead of Cu”, Solid State Commun., Vol 71, No. 8, pp. 663-668 (1989).

[5] I. Tsukada, T. Yamamoto, M. Takagi, T. Tsubone and K. Uchinokura, “Negative magnetoresistance in (Bi,Pb)$_2$Sr$_3$Co$_2$O$_9$ layered cobalt oxides”, Mat. Res. Soc. Symp. Proc., Vol.494, pp. 119-125 (1998).

[6] I. Terasaki, T. Nakahashi, A. Maeda and K. Uchinokura “Optical reflectivity of single-crystal Bi$_2$M$_3$Co$_2$O$_9$ (M=Ca, Sr and Ba) from infrared to vacuum-ultraviolet region”, Phys. Rev. B, Vol. 47, No. 1, pp. 451-456 (1993)

[7] H. Yakabe, K. Kikuchi, I. Terasaki, Y. Sasago and K. Uchinokura, “Thermoelectric propereties of transition-metal oxide NaCo$_2$O$_4$ system”, in Proceedings of the XVIth International Conference on Thermoelectrics, Dresden, Germany, August 26-29, 1997 (in press).

[8] For example, C. S. Garde and J. Ray, “Thermopower and resistivity behavior in Ce-based Kondo-lattice systems: A phenomenological approach”, Phys. Rev. B, Vol. 51, No. 5, pp. 2960-2965 (1995).

![Fig. 5](image1) (a) In-plane resistivity and (b) in-plane thermopower of single crystals of Bi$_2$M$_3$Co$_2$O$_9$ (M=Sr and Ba).

![Fig. 6](image2) (a) In-plane resistivity and (b) in-plane thermopower of single crystals of Bi$_{2-x}$Pb$_x$Sr$_3$Co$_2$O$_9$. 