

# Thermoelectric properties in $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_{3-y}\text{Y}_y\text{Co}_2\text{O}_{9-\delta}$ ceramics

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## Abstract

Thermoelectric (TE) properties (resistivity and thermopower) of polycrystalline ceramics in the  $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_{3-y}\text{Y}_y\text{Co}_2\text{O}_{9-\delta}$  system prepared by a solid-state reaction in air have been investigated as a function of temperature up to about 300 K, changing the combination of  $x$  and  $y$ . These oxides are chemically very stable, and TE properties and the lattice structures do not change even after they are heated at high temperatures. Y doping has a profound effect in reducing resistivity. When  $y$  (the amount of Y) is small, ligand holes created by O 2p–Co 3d hybridization are mainly responsible for insulating conduction. With increasing  $y$ , resistivity decreases rapidly and insulating conduction transfers to metallic conduction. This is due to the shrinkage in the lattice constant by the Y doping, which leads to band crossing of the O 2p and Co 3d levels. Measurements of TE properties including thermal conductivity have been carried out on the material with  $x = y = 0.5$  in the high-temperature range up to 800 K. The TE figure of merit increases from  $2 \times 10^{-5} \text{ K}^{-1}$  to  $7 \times 10^{-5} \text{ K}^{-1}$  as the temperature increases from 400 K to 800 K, which indicates that this compound has high potential as a good TE material at high temperatures.

## 1. Introduction

Thermoelectric (TE) materials have recently attracted renewed interest as an application to a clean energy-conversion system that utilizes the heat wasted at high temperatures [1]. The conversion efficiency of a TE material is characterized by the TE figure of merit  $Z = S^2/\rho\kappa$ , where  $S$ ,  $\rho$  and  $\kappa$  are the thermopower (Seebeck coefficient), resistivity and thermal conductivity. A good TE material involves, therefore, high thermopower and low resistivity with low thermal conductivity. However, a high magnitude for  $Z$  is difficult to realize because these parameters do not change independently. In most materials where band conduction dominates electronic transport, such as degenerate semiconductors and intermetallic compounds, the high concentration of carriers responsible for low resistivity

generally results in high thermal conductivity [2]. For this reason, materials with  $Z$  high enough for practical applications are limited to some conventional TE materials such as  $\text{Bi}_2\text{Te}_3$ ,  $\text{PbTe}$  and  $\text{SiGe}$ , their carrier concentrations being nearly equal, i.e.  $\sim 10^{19} \text{ cm}^{-3}$  [3].

The utilization of these conventional materials is unfortunately restricted within narrow limits such as a Peltier cooler. They are used either at rather low temperatures or under vacuum because they contain serious problems of oxidation, decomposition and melting at high temperature in air. TE materials applicable to a clean energy-conversion system require a function to overcome these problems. From this point of view, metal oxides have great advantages in material syntheses and also in long-term use at high temperature in air. The development of new metal oxides with high  $Z$  is then of great importance. Furthermore, the studies on oxides in the strongly correlated electron system which have been carried out dynamically after the discovery of high- $T_c$  superconducting

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oxides [4] provide detailed knowledge as to the electronic conduction yielding low resistivity, and suggest a possibility that some modulated perovskite oxides could be candidates for good TE materials [5, 6]. It is generally accepted that a hopping process of large and/or small polarons governs electronic transport in most of these oxides, which results in conduction quite different from band conduction [7, 8]. Referring to the literature on thermal conduction in  $(\text{Na}, \text{Ca})\text{Co}_2\text{O}_4$  in which thermal conductivity  $\kappa$  is mainly determined by phonons rather than electronic carriers (because  $\kappa_{ph} \simeq \kappa$  and  $\kappa_{el} < \kappa_{ph}$ , where  $\kappa_{ph}$  is thermal conductivity due to phonons and  $\kappa_{el}$  is that due to electronic carriers which is estimated using Wiedemann–Franz law [9]), one can expect a similar situation in other Co oxides. There is also a possibility to change resistivity and thermal conductivity independently in the present system because the carrier responsible for conduction is expected to differ from that for thermal conduction.

Along this line, Itoh *et al* [5] and Terasaki *et al* [10] investigated TE properties in  $\text{NaCo}_2\text{O}_4$ , one of layered cobalt oxides. The carrier concentration in  $\text{NaCo}_2\text{O}_4$  is about  $10^{21} \text{ cm}^{-3}$ , much larger than conventional TE materials. This oxide involves a large  $S$  of  $100 \mu\text{V K}^{-1}$  and a low  $\rho$  of  $200 \mu\Omega \text{ cm}$  with a low  $\kappa$  of  $15 \text{ mW cm}^{-1} \text{ K}^{-1}$  at room temperature [5, 10–12]. These numerical parameters yield a large magnitude for  $Z$  in comparison with other oxides. Then  $\text{NaCo}_2\text{O}_4$  has surely high potential as a good TE material.

The present study treats  $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_{3-y}\text{Y}_y\text{Co}_2\text{O}_{9-\delta}$ , which is believed to have a structure nearly isomorphous to  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  (BSCCO; one of high- $T_c$  superconductors), i.e.  $n = 2$  layered perovskite structure [13]. In the recent work by Yamamoto *et al* [14], the (Bi, Pb)–Sr–Co–O system has a misfit structure which results from bidimensional matching of two different structures, such as rock-salt-type layers and hexagonal- $\text{CdI}_2$ -type layers.

$\text{Pb}^{2+}$  substitution for  $\text{Bi}^{3+}$  leads to hole-doping, which increases the amount of holes; the majority carrier in the present system. However, the large difference in ionic radii of  $\text{Bi}^{3+}$  and  $\text{Pb}^{2+}$  may bring about some unexpected changes on the TE properties. Pb doping in Bi–Sr–Co–O system has been investigated in detail [5, 6, 14–16]. There is however little knowledge as to Y effects, although one expects electron doping by  $\text{Y}^{3+}$  substitution for  $\text{Sr}^{2+}$ . It is therefore very significant to investigate the effect of Y on the TE properties in the (Bi, Pb)–Sr–Co–O system.

As for  $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_3\text{Co}_2\text{O}_9$ , Shin and Murayama [6] produced hot-pressure-sintered samples besides the normal pressure-sintered ones, like those in the present study, and Itoh *et al* [5] carried out TE experiments on single crystals. The TE results obtained by both groups are very important in examining the reliability of our experiment and also in discussing effect of Y on TE properties.

The development of a new highly efficient TE material applicable to the utilization at high temperature in air requires a simple production process. From this point of view, the present study concentrates on preparing polycrystalline ceramics sintered in air. Based upon such a strategy, resistivity, thermopower and magnetic susceptibility for  $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_{3-y}\text{Y}_y\text{Co}_2\text{O}_{9-\delta}$  ceramics were measured as functions of temperature at  $T \lesssim 300 \text{ K}$ , changing the combination of  $x$  and  $y$  (i.e. the amounts of substitutes Pb

and Y), and we have tried to obtain the best combination of  $x$  and  $y$  for a TE material in this system. The TE properties of the specimen with the best combination of  $x$  and  $y$  were also investigated in the high-temperature region above 300 K. Furthermore, the transport properties are discussed in terms of the electron states varied by Y substitution.

## 2. Experiments

$\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_{3-y}\text{Y}_y\text{Co}_2\text{O}_{9-\delta}$  polycrystalline ceramics specimens were prepared by a conventional solid-state synthesis technique. Bismuth oxide ( $\text{Bi}_2\text{O}_3$ ), lead dioxide ( $\text{PbO}_2$ ), strontium carbonate ( $\text{SrCO}_3$ ), yttrium oxide ( $\text{Y}_2\text{O}_3$ ) and tri-cobalt tetra-oxide ( $\text{Co}_3\text{O}_4$ ) powders were used (4 N). The present study changes  $x$  from 0.3 to 0.7 and  $y$  from 0.0 to 0.7. First, mixed powders were calcined in air at  $790\text{--}840^\circ\text{C}$  for 12–24 h in air. The heating temperature and time depended on the combination of  $x$  and  $y$ . After being ground very carefully and mixed well, powders were pressed into pellets and finally sintered in air at  $840\text{--}870^\circ\text{C}$  for 1 day.

After investigating lattice structures by Cu  $K\alpha$  x-ray diffraction (XRD), the four-probe dc resistivity and thermopower (Seebeck coefficient) in the low-temperature region up to room temperature were measured in the following way. A Keithley 619 resistance bridge, an Advantest TR 6871 digital multimeter and an Advantest R 6161 power supply were used for dc-resistivity measurements. Thermopower measurement was carried out on a sample placed between two blocks of oxygen-free high conductivity (OFHC) copper. Both ends of the sample were coated with platinum paste and then placed in contact with thin copper plates. Copper–constantan thermocouples were welded to the reverse sides of the copper plates to measure temperature and thermopower. The temperature difference between both ends of a specimen was 10–15 K. The magnetic susceptibilities,  $\chi$ , were measured with the magnetic field of 0.1 T by a SQUID (Quantum Design MPMS) in the temperature range of 10 K to 300 K.

Thermopower, resistivity and thermal conductivity in the high-temperature region above 300 K were measured as functions of temperature for the specimen of  $x = y = 0.5$  because this combination has the best TE characteristic below room temperature. Using Pt leads (0.05 mm diameter), four-probe dc resistivity was obtained under vacuum at 100 K increments up to about 800 K. A Pt–Pt(13% Rh) thermocouple was used to measure the temperature. The thermopower was also measured under vacuum using microheaters attached near both ends of a specimen. Maintaining the average temperature of the specimen at each measurement temperature, different voltages were applied to these microheaters individually. The voltage ratio changed from 1/99 to 99/1, and totally 100 ratios were employed. The change in the voltage ratio varied the temperature difference between the ends of the specimen  $\Delta T$  from +2 K to –2 K. In each voltage ratio, the potential difference between the ends of the specimen  $\Delta V$  was measured. The slope ( $d\Delta V/d\Delta T$ ) obtained by the least-squares method over 100 plots yields thermopower  $S$  at each measurement temperature. The laser flash method (Rigakudenki LF/TCM-FA8510B) measured thermal diffusivity under vacuum. The thermal conductivity  $\kappa$  was then calculated using the experimental values for thermal diffusivity  $D$ , specific heat capacity  $C$  and the density of the specimen.

### 3. Results and discussion

#### 3.1. Lattice structure

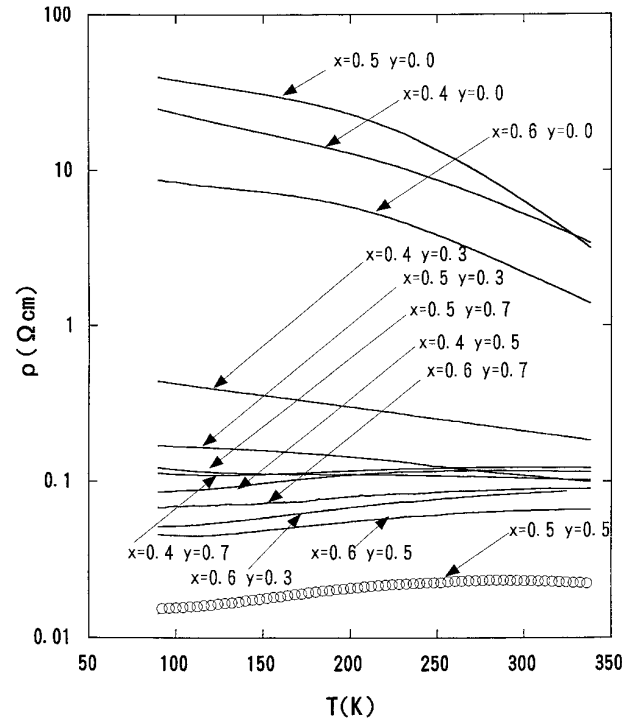
The main XRD pattern of  $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_{3-y}\text{Y}_y\text{Co}_2\text{O}_{9-\delta}$  prepared in the present study agrees with that in  $\text{Bi}_2\text{Sr}_3\text{Co}_2\text{O}_9$  reported by Tarascon *et al* [13] and Tsukada *et al* [14, 15]. In addition to the main XRD pattern there are satellite peaks that are not involved in the XRD pattern of  $\text{Bi}_2\text{Sr}_3\text{Co}_2\text{O}_9$  single crystal. In ceramics sample of  $\text{Bi}_2\text{Sr}_3\text{Co}_2\text{O}_9$ , however, the XRD pattern does involve these satellite lines [6, 14, 16]. As described in the introduction, Yamamoto *et al* indexed the XRD pattern including the satellite lines based upon the misfit structure coming from bidimensional matching of two different structures of rock-salt-type layers and hexagonal- $\text{CdI}_2$ -type layers, see [14, 17]. The previous literature argues that the  $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_3\text{Co}_2\text{O}_9$  ceramic is not a single phase and that impurity phases such as  $\text{Bi}_2\text{Sr}_2\text{O}_5$  and  $\text{SrCoO}_y$  segregate along the boundaries [18]. The volume fractions of these impurity phases must be very small in comparison with the main phase, even if they are involved in the present system. It is worth noting that even  $\text{Bi}_2\text{Sr}_3\text{Co}_2\text{O}_9$  contains impurity phases if produced by a solid-state reaction like ours [6, 19]. The present experiment shows that the lattice constant along  $c$ -axis in  $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_{3-y}\text{Y}_y\text{Co}_2\text{O}_{9-\delta}$  shrinks as the amount of Y increases. This is due to the ionic radius of  $\text{Y}^{3+}$  being smaller than that of  $\text{Sr}^{2+}$ .

An attempt to eliminate the satellite lines in the XRD pattern using flowing nitrogen gas (a reducing atmosphere) in calcinations of mixed powders at temperatures lower than 790–840 °C was tried, but proved unsuccessful. Tsukada *et al* [19] succeeded in eliminating these lines by preparing  $\text{Bi}_2\text{Sr}_{3-z}\text{Co}_2\text{O}_w$  with  $z$  varying from 0.0 to 1.0, where  $w$  represents the unknown content of oxygen which must deviate from the stoichiometric value, i.e. 9. They employed a solid-state reaction. As  $z$  increased, the satellite lines decayed and are finally annihilated at  $z = 1.0$ , i.e.  $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_w$ . The main XRD pattern in  $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_w$  agrees with the present system,  $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_{3-y}\text{Y}_y\text{Co}_2\text{O}_{9-\delta}$ . However, it seems rather difficult to substitute  $\text{Y}^{3+}$  for  $\text{Sr}^{2+}$  in  $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_w$  even if the amount of  $\text{Y}^{3+}$  is small. This must be due to a narrow range solubility of  $\text{Y}^{3+}$  ions in  $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_w$ .

$\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_{3-y}\text{Y}_y\text{Co}_2\text{O}_{9-\delta}$  ceramics prepared in this way are chemically very stable in air, and do not exhibit any ageing. Furthermore, the lattice structures and TE properties ( $\rho$  and  $S$ ) do not change even after the specimens were heated for 1 day at 800 K in air. This fact implies that the compounds in the present system are very stable at high temperature.

#### 3.2. Resistivity

Figure 1 demonstrates the relation of the four-probe dc resistivity  $\rho$  and temperature  $T$  below 340 K for every specimen. This figure omits the results for the  $x = 0.3$  and 0.7 series which involve high resistivity in comparison with other series, being inadequate for use as a TE material. As  $y$  increases at every  $x$ , resistivity decreases rapidly, becomes a minimum at  $y = 0.5$  and then increasing. Below room temperature, insulating conduction takes place when  $y$  is small ( $y \leq 0.3$  at  $x = 0.4$  and 0.5 and  $y = 0.0$  at  $x = 0.6$ ). With increasing  $y$ , metallic conduction or a metal–insulator (MI)



**Figure 1.** Resistivity  $\rho$  against  $T$ . The result for each specimen is represented by a full curve, except the specimen with  $x = y = 0.5$  which is shown by data points (circles).

transition occurs. As shown in figure 1, the specimen with  $x = y = 0.5$  has the minimum resistivity below 340 K.

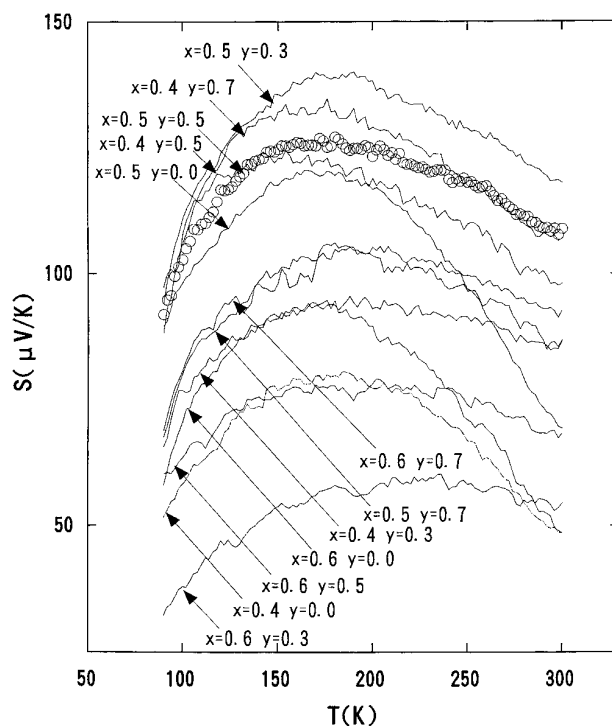
First of all, the relevance of the results obtained here should be examined. Shin and Murayama [6] produced the normal pressure-sintered  $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_3\text{Co}_2\text{O}_{9-\delta}$  samples ( $x = 0.0$  and 0.4) like ours, and hot pressure-sintered samples. They investigated the TE properties of these samples in the temperature range 440–1060 K. The resistivity of their sample with  $x = 0.4$  was compared with our Y-free sample ( $x = 0.4$  and  $y = 0.0$ ). The resistivity of their normal pressure-sintered sample at 440 K is approximately 1  $\Omega$  cm which is nearly equal to the resistivity estimated by extrapolating the resistivity plots below room temperature in the present study. In the case of the hot pressure-sintered sample, however, resistivity at 440 K is approximately 0.02  $\Omega$  cm; the reduction being about two orders of magnitude in comparison with the normal pressure-sintered sample. They ascribed such a large reduction to the bulk density. In fact, the bulk density varies from 4.49  $\text{g cm}^{-3}$  (normal press method) to 6.35  $\text{g cm}^{-3}$  (hot press method). In our Y-free samples, i.e.  $y = 0.0$ , the bulk density is 4.66  $\text{g cm}^{-3}$  at  $x = 0.4$  and 4.89  $\text{g cm}^{-3}$  at  $x = 0.5$ . The Y-free single crystal of  $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_3\text{Co}_2\text{O}_9$  ( $x = 0.4$  and  $y = 0.0$ ) produced by Itoh *et al* has a resistivity lower than ours by about three orders of magnitude [5]. The in-plane resistivity and the high bulk density in the single crystal cause such a large resistivity difference between the single crystal and the sintered ceramics.

As shown in figure 1, at every  $x$ , resistivity reduces rapidly by more than three orders of magnitude, and insulating conduction transfers to metallic conduction when  $y$  increase from 0.0 to 0.5. Referring to the result of Shin and

Murayama [6], one could expect that such a large reduction might be ascribed to an increase in the bulk density due to Y substitution, but this is denied because the bulk density decreases from  $4.89 \text{ g cm}^{-3}$  to  $4.60 \text{ g cm}^{-3}$  when  $y$  increases from 0.0 to 0.5 at  $x = 0.5$ . There is anxiety that holes doped by  $\text{Pb}^{2+}$  substitution for  $\text{Bi}^{3+}$  may be compensated by electron doping due to  $\text{Y}^{3+}$  substitution for  $\text{Sr}^{2+}$  and the concentration of holes responsible for electronic conduction may decrease, yielding a less conductive material. The result in figure 1 denies this anxiety. The holes doped by Pb substitution enhance the electronic conduction. In fact, resistivity at  $T \geq 300 \text{ K}$  decreases as  $x$  (the amount of Pb) increases when  $y = 0.0$  and  $0.3$ . However, the reduction of resistivity due to Pb substitution is considerably smaller compared to the reduction due to Y substitution [5, 14, 15]. This fact is likely to indicate that the ligand holes created by hybridization of O 2p and Co 3d  $e_g$  wavefunctions are mainly responsible for electronic conduction. It should be emphasized that this hybridization is possible because Y doping suppresses a decrease in the amount of  $\text{Co}^{3+}(t_{2g}^6)$  ions.  $\text{Y}^{3+}$  ions substituted for  $\text{Sr}^{2+}$  play a very important role in electronic conduction by stabilizing low-spin  $\text{Co}^{3+}(t_{2g}^6)$  ions. At  $y = 0.0$ , the resistivity in the specimen with  $x = 0.5$  is higher than the oxide with  $x = 0.4$  below room temperature. This must be because the activation energy required for conduction in the specimen with  $x = 0.5$  is higher than that with  $x = 0.4$ .

Referring to the transport properties of other Co oxides in the strongly correlated electron system [20–22], a hopping process of small polarons of ligand holes is expected to dominate insulating conduction when  $y$  is small. The transition from an insulator to a metal with increasing  $y$  implies, however, that the hopping process is no longer the main kinetics that governs the transport properties when  $y$  is large. As described in the previous section, Y doping shrinks the lattice constant along the  $c$ -axis. In the case of  $x = 0.4$ , the lattice constant decreases from  $14.862 \text{ \AA}$  to  $14.756 \text{ \AA}$  with increasing  $y$ , from 0.0 to 0.5, if based upon the misfit structure [14] or from  $29.726 \text{ \AA}$  to  $29.512 \text{ \AA}$  if the BSCCO structure is accepted [13], and where (00 $l$ ) XRD patterns are employed in these estimations. The shrinkage in the lattice constant due to Y doping must lead to band crossing of O 2p and Co 3d  $e_g$  levels and then rather wide bands must be formed. Metallic conduction with high mobility is easily realized in rather wide bands. Y doping has a very important effect on the reduction of resistivity through the shrinkage in the lattice constant. Furthermore, Y ions may relax the lattice distortion due to Pb substitution and this would be one of the reasons that reduce resistivity in Y-doped specimens, because a less deformed lattice enhances electronic conduction. At every  $x$ , the relation of resistivity and  $y$  indicates that there is an optimum magnitude for  $y$ , i.e.  $y = 0.5$ , and an excess amount of Y ions has a negative effect on the reduction of resistivity. A narrow range of solubility of  $\text{Y}^{3+}$  in the (Bi, Pb)–Sr–Co–O system must bring about this negative effect. The speculation over the resistivity result in figure 1 indicates that Y substitution is indispensable, as well as Pb substitution, for the development of a good TE compound using the present system.

Since our specimens were sintered in air, there is anxiety that electron doping due to oxygen deficiency may counterbalance hole doping by Pb substitution even if  $y = 0.0$ .



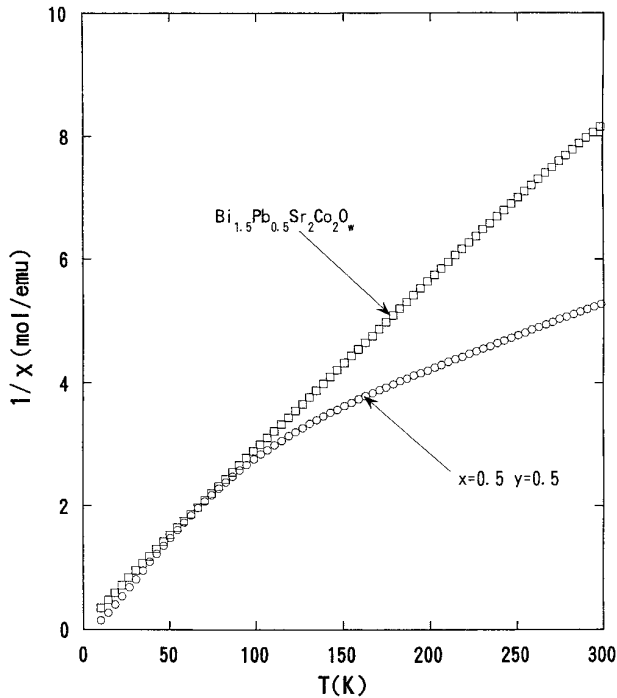
**Figure 2.** Thermopower  $S$  against  $T$ . The result for each specimen is represented by a full curve, except the specimen with  $x = y = 0.5$  which is shown by data points (circles).

New specimens were prepared in flowing oxygen gas and the resistivity was measured. In comparison with the specimens sintered in air, the resistivity decreases; but only very slightly, the reduction being less than 20%. Therefore, the oxygen-deficient effect does not have such a significant effect on resistivity as Y substitution.

As shown in figure 1, an MI transition takes place at  $280 \text{ K}$  in the specimen with  $x = y = 0.5$ , i.e.  $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_{2.5}\text{Y}_{0.5}\text{Co}_2\text{O}_{9-\delta}$ . The decrease in resistivity with increasing temperature at  $T \geq 280 \text{ K}$ , even very slow, is of great advantage to a TE material at high temperature. Referring to the previous literature [18], impurity phases such as  $\text{Bi}_2\text{Sr}_2\text{O}_5$  and  $\text{SrCoO}_y$  may also segregate along boundaries in the present system. Despite these segregations,  $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_{2.5}\text{Y}_{0.5}\text{Co}_2\text{O}_{9-\delta}$  has high potential for use as a TE material because of its low resistivity.

### 3.3. Thermopower

Figure 2 plots thermopower  $S$  against  $T$  below  $300 \text{ K}$  for every specimen. Despite rapid variations in resistivity over several orders by changing the combination of  $x$  and  $y$ , the thermopower in every specimen is within the same order of magnitude. Although this fact seems to indicate that, in the present system, the thermopower has a less profound effect upon the figure of merit,  $Z$ , compared with resistivity, thermopower is also very important because the figure of merit is proportional to the square of the thermopower. A positive thermopower indicates that the majority carrier in the present system is a hole as expected, despite electron doping by Y substitution.



**Figure 3.** Inverse molar magnetic susceptibility  $\chi^{-1}$  against  $T$  for the specimen with  $x = y = 0.5$  (open circles) and  $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{Co}_2\text{O}_w$  (open squares).

As the temperature increases, the thermopower in every specimen increases to a maximum at around 180 K and then decreases. A temperature dependence of the thermopower like this is observed in many insulating oxides [23, 24]. Although there is no evidence to indicate that such thermopower behaviour is peculiar to an insulator, it is interesting that a similar result is even obtained in the specimen with  $x = y = 0.5$ , which exhibits the MI transition at 280 K. If this compound is to be used as a TE material at high temperature, the measurement of thermopower above 300 K would be indispensable because such a decrease in thermopower with increasing temperature is never an advantage to a TE material at high temperatures. The magnitudes for  $S$  at room temperature in the present system are competitive with the thermopower of single crystals of  $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_3\text{Co}_2\text{O}_9$  [5] and are a little larger than  $\text{Na}_{1-x}\text{Ca}_x\text{Co}_2\text{O}_4$  [11]. According to Shin and Murayama [6], thermopower is not as sensitive to the bulk density as resistivity.

Since Koshibae *et al* [25] theoretically predict that a large magnitude for  $S$  requires low-spin Co ions, the magnetic susceptibility,  $\chi$ , in the present system has been measured so as to elucidate the spin structure of the Co ions. Figure 3 depicts the temperature dependence of the inverse molar magnetic susceptibility  $\chi^{-1}$  for  $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_{2.5}\text{Y}_{0.5}\text{Co}_2\text{O}_{9-\delta}$  ( $x = y = 0.5$ ). Other specimens exhibit the similar behaviours. Around 100 K there is a sudden change in the slope  $d\chi^{-1}/dT$  and the Curie–Weiss relation seems difficult to hold even above 100 K. This complex feature was unexpected and it seems difficult to estimate an effective magnetic moment. Either a change in the spin structure of the Co ions or impurity phases such as  $\text{Bi}_2\text{Sr}_2\text{O}_5$  and  $\text{SrCoO}_y$  must be responsible for such an anomaly at 100 K.

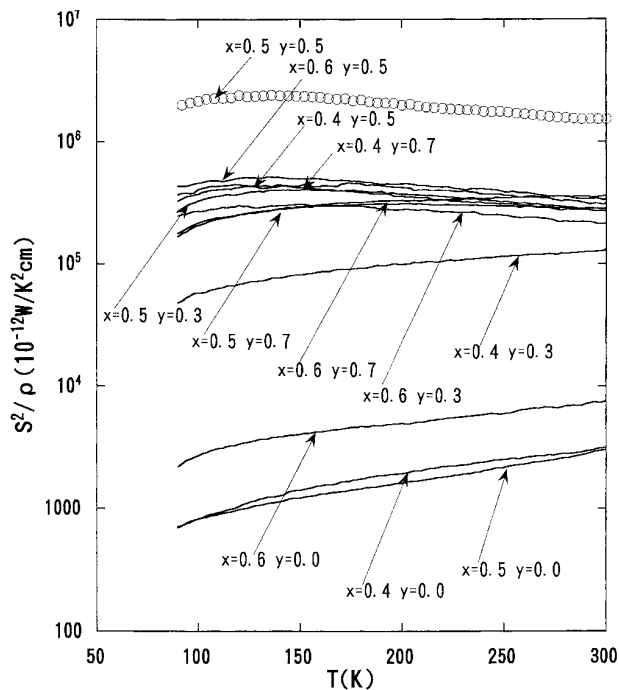
For reference, the plots of  $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{Co}_2\text{O}_w$  prepared in the present study are also shown in figure 3. The Curie–Weiss law holds above 10 K, although this compound involves a ferromagnetic–paramagnetic transition around 4 K [15, 16]. The straight line in the Curie–Weiss relation indicates that the spin structure of the Co ions never changes in  $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{Co}_2\text{O}_w$  below room temperature. In the Curie–Weiss relation in the paramagnetic regime above 10 K, the experimental magnitude for the Curie constant ( $C \cong 0.03 \text{ emu K mol}^{-1}$ ) yields  $\mu_{eff} \cong 0.45 \mu_B$  under the assumption that  $w \cong 9$ , where  $\mu_{eff}$  and  $\mu_B$  are the effective magnetic moment and the Bohr magneton. This effective magnetic moment estimates that about 90% of the Co ions are low-spin  $\text{Co}^{3+}$  ( $t_{2g}^6$ ;  $S = 0$ ) and the remainder are low-spin  $\text{Co}^{4+}$  ( $t_{2g}^5$ ;  $S = 1/2$ ). Referring to the speculation on  $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{Co}_2\text{O}_w$ , the spin structure of the Co ions in  $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_{3-y}\text{Y}_y\text{Co}_2\text{O}_{9-\delta}$  system must be rather hard to change, and there is a possibility that compounds in this system contain mostly low-spin Co ions. In fact,  $\text{Y}^{3+}$  substitution for  $\text{Sr}^{2+}$  stabilizes low-spin  $\text{Co}^{3+}$  ( $t_{2g}^6$ ;  $S = 0$ ) because electrons doped by this substitution suppress the creation of  $\text{Co}^{4+}$  ( $t_{2g}^5$ ;  $S = 1/2$ ) due to  $\text{Pb}^{2+}$  substitution for  $\text{Bi}^{3+}$ . If impurity phases are the main reason for the complex magnetic behaviour in  $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_{2.5}\text{Y}_{0.5}\text{Co}_2\text{O}_{9-\delta}$  as shown in figure 3, Co ions in  $\text{SrCoO}_y$  must be mainly responsible because other ions in  $\text{Bi}_2\text{Sr}_2\text{O}_5$  and  $\text{SrCoO}_y$  do not contain the 3d electrons which govern magnetic properties.

The suggestion made by Yamamoto *et al* [14] is very noteworthy. They emphasize that the hexagonal- $\text{CdI}_2$ -type layers ( $\text{CoO}_2$  layers) in the misfit structure, which they proposed, are similar to that in  $\text{NaCo}_2\text{O}_4$  [12] and the large thermopower in both  $\text{NaCo}_2\text{O}_4$  and  $\text{Bi-Sr-Co-O}$  system may be related to this common structure. In fact, the spin structure of a Co ion depends very sensitively upon the relative positions of the  $\text{O}^{2-}$  ions around that Co ion. Not only the large thermopower but also the low resistivity must have some correlation with the hexagonal- $\text{CdI}_2$ -type layers, which could be the key structure in the development of good TE materials.

### 3.4. TE properties of $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_{2.5}\text{Y}_{0.5}\text{Co}_2\text{O}_{9-\delta}$ above 300 K

Since the power factor  $S^2/\rho$  is one of the measures for a good TE material, figure 4 plots  $S^2/\rho$  against  $T$  for every specimen. In the present system the combination of  $x = y = 0.5$  is the best one, and has a power factor that is larger than the next best ( $x = 0.5$  and  $y = 0.3$ ) by approximately one order of magnitude. Measurement of resistivity, thermopower and thermal conductivity have been carried out on this specimen ( $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_{2.5}\text{Y}_{0.5}\text{Co}_2\text{O}_{9-\delta}$ ) in the high-temperature region above 300 K.

Figure 5(a) plots  $\rho$  against  $T$ . As expected from the MI transition around 280 K, the resistivity seems to decrease monotonously as the temperature increases, except the plot at 500 K. The relation between  $S$  and  $T$  is illustrated in figure 5(b). As shown in figure 2, thermopower in this specimen has a maximum around 180 K and then decreases as temperature increases towards 300 K. Above 300 K, the thermopower also keeps decreasing to a minimum around 400 K and then increases again with temperature. Although it is still unknown why the thermopower increases at  $T \geq 400$  K,



**Figure 4.** Power factor  $S^2/\rho$  against  $T$ . The result for each specimen is represented by a full curve, except the specimen with  $x = y = 0.5$  which is shown by data points (circles).

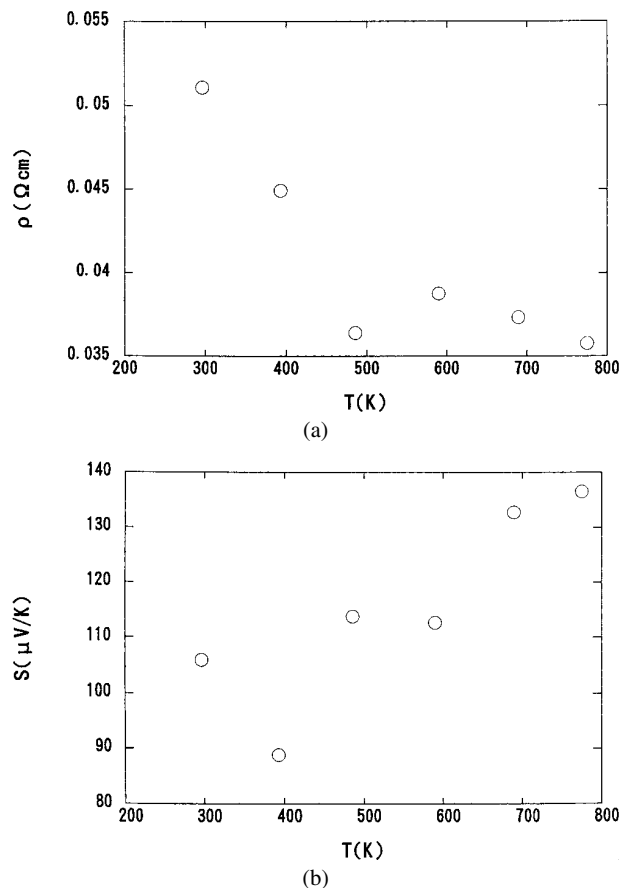
**Table 1.** Thermal diffusivity  $D$ , specific heat capacity  $C$  and thermal conductivity  $\kappa$  at  $T = 300$  K, 400 K, 600 K and 800 K for the specimen with  $x = y = 0.5$ .

$T$ (K)	$D$ ( $\text{cm}^2 \text{s}^{-1}$ )	$C$ ( $\text{J g}^{-1} \text{K}^{-1}$ )	$\kappa$ ( $\text{mW cm}^{-1} \text{K}^{-1}$ )
300	0.0065	0.32	10.0
400	0.0059	0.34	9.0
600	0.0052	0.32	8.0
800	0.0049	0.34	8.0

such an increase is of great advantage to a TE material at high temperatures. Since the thermopower has a singular point at 500 K as well as resistivity, a magnetic or lattice transformation might occur around 500 K. These results suggest that  $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_{2.5}\text{Y}_{0.5}\text{Co}_2\text{O}_{9-\delta}$  could be a good TE material at high temperature.

The thermal conductivity  $\kappa$  at each temperature was estimated using the experimental magnitudes for thermal diffusivity  $D$  and specific heat capacity  $C$  summarized in table 1; the bulk density of  $4.60 \text{ g cm}^{-3}$  previously obtained was used as the density of the specimen with  $x = y = 0.5$ . Figure 6(a) depicts the relation of  $\kappa$  and  $T$ . At room temperature,  $\kappa \cong 10.0 \text{ mW cm}^{-1} \text{K}^{-1}$ . This is lower than  $\text{NaCo}_2\text{O}_4$ . The thermal conductivity decreases with increasing  $T$ . It is an advantage to use  $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_{2.5}\text{Y}_{0.5}\text{Co}_2\text{O}_{9-\delta}$  as a TE material at high temperature because the TE figure of merit is proportional to the inverse thermal conductivity,  $\kappa^{-1}$ .

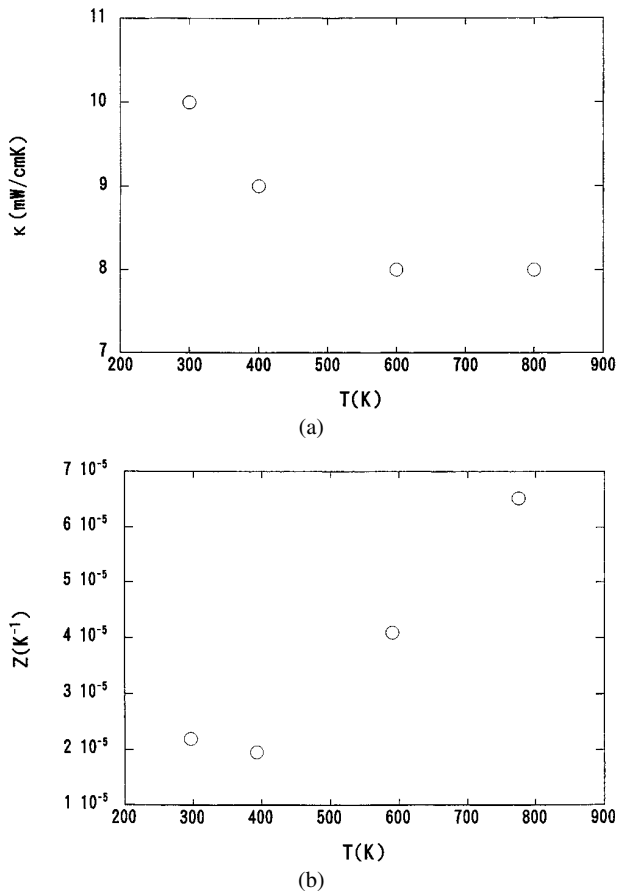
The figure of merit for  $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_{2.5}\text{Y}_{0.5}\text{Co}_2\text{O}_{9-\delta}$  increases monotonously from  $2 \times 10^{-5} \text{ K}^{-1}$  to  $7 \times 10^{-5} \text{ K}^{-1}$  as temperature rises from 400 K to 800 K, as shown in figure 6(b). In comparison with conventional TE materials such as  $\text{Bi}_2\text{Te}_3$  and  $\text{PbTe}$  [26],  $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_{2.5}\text{Y}_{0.5}\text{Co}_2\text{O}_{9-\delta}$  is very resistant against oxidation at high temperature.



**Figure 5.** Plots of (a)  $\rho$  against  $T$  and (b)  $S$  against  $T$  in the temperature range of 300–800 K for the specimen with  $x = y = 0.5$ .

$\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_{2.5}\text{Y}_{0.5}\text{Co}_2\text{O}_{9-\delta}$  has a magnitude for  $Z$  competitive with other oxides such as  $(\text{ZnO})_5(\text{In,Y})_2\text{O}_3$  and  $\text{Ca}(\text{Mn,In})\text{O}_3$  above 500 K [27, 28], and is rather superior to  $(\text{La,Sr})\text{CrO}_3$  and  $(\text{Nd,Ce})_2\text{CuO}_4$  [29, 30]. Since  $\text{Na}(\text{Co,Cu})_2\text{O}_4$  has a magnitude for  $Z$  larger than  $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_{2.5}\text{Y}_{0.5}\text{Co}_2\text{O}_{9-\delta}$  by one order of magnitude [31],  $\text{Na}(\text{Co,Cu})_2\text{O}_4$  is surely a strong candidate for use as a TE material. However,  $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_{2.5}\text{Y}_{0.5}\text{Co}_2\text{O}_{9-\delta}$  is chemically stable and very resistant against degradation during long-term use in air at high temperatures as described above. This oxide could then be a good TE material at high temperatures.

The development of  $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_{3-y}\text{Y}_y\text{Co}_2\text{O}_{9-\delta}$  ceramics as a practical TE material requires several improvements. As described above,  $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_{2.5}\text{Y}_{0.5}\text{Co}_2\text{O}_{9-\delta}$  has a thermal conductivity and thermopower comparable to  $\text{NaCo}_2\text{O}_4$ , but its resistivity is larger than  $\text{NaCo}_2\text{O}_4$  by one or two orders of magnitude. A  $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_{3-y}\text{Y}_y\text{Co}_2\text{O}_{9-\delta}$  system would be a very strong TE material if its resistivity is decreased. To this end, its electronic transport properties, including conduction kinetics, should be elucidated in more detail. Furthermore, the use of lead is not desirable from an environmental point of view. It would be best if the lead is replaced with other elements, but this replacement should improve the TE properties.



**Figure 6.** Plots of (a) the thermal conductivity  $\kappa$  against  $T$  and (b) the TE figure of merit  $Z$  against  $T$  in the temperature range of 300–800 K for the specimen with  $x = y = 0.5$ .

#### 4. Conclusions

The TE properties (resistivity and thermopower) of  $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_{3-y}\text{Y}_y\text{Co}_2\text{O}_{9-\delta}$  system have been investigated below room temperature, by changing the combination of  $x$  and  $y$ . These oxides are chemically very stable, do exhibit ageing and are very resistant against degradation during long-term use at high temperature. At every  $x$ , the resistivity decreases rapidly by more than three orders of magnitude and insulating conduction transfers to metallic conduction as  $y$  (the amount of Y ions) increases from 0.0 to 0.5; it is the variation of the electron states due to Y doping that mainly causes these results. The ceramic compound with  $x = y = 0.5$  was found to have the best TE properties in the present system. The measurements of resistivity, thermopower and thermal conductivity were carried out on this compound ( $x = y = 0.5$ ) in the high-temperature range up to 800 K, and the figure of merit increases from  $2 \times 10^{-5} \text{ K}^{-1}$  to  $7 \times 10^{-5} \text{ K}^{-1}$  as temperature increases from 400 K to 800 K. The magnitude of the figure of merit such as this is competitive with other TE oxides. Though Pb substitution dopes holes, the ligand holes created by O 2p–Co 3d  $e_g$  hybridization are mainly responsible for electronic conduction when the amount of Y is small. The Y substitution assures this hybridization because this substitution suppresses the destabilization of the low-spin  $\text{Co}^{3+}$  ( $t_{2g}^6$ ;  $S = 0$ ) ions which the ions created by  $\text{Co}^{4+}$  ( $t_{2g}^5$ ;  $S = 1/2$ ) Pb substitution cause.

As the amount of Y increases, Y substitution for Sr decreases resistivity through shrinkage in the lattice constant along the  $c$ -axis, leading to band crossing of O 2p and Co 3d  $e_g$  levels and to the partial removal of lattice deformation produced by Pb substitution because a less deformed lattice enhances electronic conduction.

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