Abstract
In-plane anisotropy of the resistivity and thermopower was measured for single crystal Bi$_{2-x}$Pb$_x$Sr$_2$Co$_2$O$_{y}$. There is large in-plane anisotropy, which is attributed to the anisotropic pseudogap formation due to the different crystal symmetry between the square Bi$_2$Sr$_2$O$_4$ layer and the triangular CuO$_2$ layer. The magnitude of the thermopower both along $a$- and $b$-axis direction increases with Pb doping from $x=0$ to $0.4$, where we observe discontinuous shrink of $b$-axis length. We attribute this to the enhancement of the misfit. Thus, we can improve the thermoelectric properties by tuning the misfit.

Introduction
Since NaCoO$_2$ is found to show large thermopower (100 $\mu$V/K at 300 K) and low resistivity (200 $\mu$Ωcm at 300 K) [1], the layered Co oxides are expected to be a candidate for thermoelectric materials [2-5]. They are characterized by a two-dimensional CoO$_2$ layer, which consists of edge-shared CoO$_6$ octahedra responsible for the electric conduction and the large thermopower. Among them, Bi$_2$Sr$_2$CoO$_4$ was first thought to have a structure isomorphic to that of the high-$T_c$ Cu oxide Bi$_2$Sr$_2$CaCu$_2$O$_{8+}$ (Bi-2212) because these two compounds have almost same lattice constants. However, it turned out to be a “misfit compound”, where the rock-salt type square Bi$_2$Sr$_2$O$_4$ layer lies on the CdI$_2$-type triangular CoO$_2$ layer with lattice misfit along the $b$ axis [6]. Another striking feature of the crystal structure in the Bi based layered oxides, is modulation structure [7], which disappears by the substitution of Bi by Pb [8].

From the viewpoint of the group theory, the hexagonal CoO$_2$ layer in Bi$_2$Sr$_2$CoO$_4$ and the square CuO$_2$ layer in Bi-2212 themselves should have no in-plane anisotropy in the thermopower and resistivity. However, in some cases, in-plane anisotropy in the resistivity can be observed [9]. A possible origin of the in-plane anisotropy is the self-organization of the electronic system into quasi-one-dimensional stripes. The enhancement of the in-plane anisotropy of the resistivity $\rho_{ab}/\rho_{c}$ has been reported in the lightly doped high-$T_c$ Cu oxide La$_{2-\delta}$Sr$_{\delta}$CuO$_4$ and YBa$_2$Cu$_3$O$_y$, and has been associated with the charge-stripe [10].

In the case of the Bi$_2$Sr$_2$CoO$_4$, the coupling between the square Bi$_2$Sr$_2$O$_4$ layer and the triangular CoO$_2$ layer is considered to be strong. Then, the stack of different symmetry layers would induce the in-plane anisotropy in the physical properties. Moreover, the lattice misfit between these two layers is thought to induce chemical pressure along the $b$-axis direction. It is, then, interesting how the electric properties are affected by these misfit structures. Here, we have grown the large single crystal of Bi$_{2-x}$Pb$_x$Sr$_2$CoO$_y$ by using traveling solvent floating zone (TSFZ) method, and have measured the in-plane anisotropy on the resistivity and thermopower.

Experimental
Single crystals of Bi$_{2-x}$Pb$_x$Sr$_2$CoO$_y$ ($x=0$, 0.4, and 0.6) were grown by TSFZ method at a growth rate of 0.5 mm/h in a mixed gas flow of O$_2$ (20%) and Ar (80%). The starting compositions for all Pb concentrations were applied (Bi,Pb) : Sr : Co = 2 : 2 : 2. Large single crystals with dimensions up to $5*4*0.5$ mm$^3$ were successfully grown.

The grown crystals were characterized by a four-circle x-ray diffractometer (Cu K$_\alpha$ x-ray source) and a transmission electron microscope (TEM). The actual composition was analyzed through inductively coupled plasma-atomic emission spectroscopy (ICP) and energy dispersive x-ray analysis (EDX). $a$- and $b$-axis resistivities were measured by a standard four-probe method using different samples cleaved along $a$- and $b$-axis directions. $a$- and $b$-axis thermopowers were measured by a steady-state technique using the same sample changing the measurement configurations.

Results and Discussion
Samples used for this study are listed in Table 1 with the actual chemical compositions. Hereafter, we refer to these samples as nominal Pb concentration. The actual compositions of Pb measured by ICP and EDX correspond well with the nominal compositions. We analyze several samples for each Pb concentration, and confirm the homogeneity of the samples.

Since Bi$_{2-x}$Pb$_x$Sr$_2$CoO$_y$ has very complicated structure as explained above, it was difficult to perform single-crystal structure analysis. We manually searched the diffraction peak using the reported lattice constants. The obtained lattice

| x | Bi   | Pb  | Sr   | Co |
|---|------|-----|------|----|
| 0 | EDX | 2.21| 0    | 2.20| 2.0 |
|   | ICP | 2.10| 0    | 2.10| 2.0 |
| 0.4| 1.60| 0.40| 2.09 | 2.0 |
| 0.6| 1.82| 0.42| 2.18 | 2.0 |
|    | 1.58| 0.57| 2.13 | 2.0 |
|    | 1.60| 0.60| 2.10 | 2.0 |
parameters are shown in Fig. 1 plotted against actual composition. The data from the previous report are also shown [11], where the lattice constants were estimated from a powder XRD measurement using crushed single crystals. These results well correspond to each other. Since Co atoms have large mass absorption coefficient for Cu Kα radiation, observed reflections come from the rock-salt Bi₂Sr₂O₅-layer. Thus, we refer a- and b-axis lengths obtained here as \(a_{RS}\) and \(b_{RS}\)-axis. The c-axis length monotonically increases with increasing Pb concentration due to the large ion radius of Pb. Note that the \(b_{RS}\)-axis length discontinuously shrinks with Pb concentration from \(x=0\) to 0.4. While, the \(d_{RS}\)-axis length does not change with Pb concentration.

**Figure 1.** The lattice parameter characterized by a four-circle x-ray diffractometer. Previous data estimated from powder x-ray diffractometer using crushed single crystals is also shown.

Figures 2(a) and (b) show the TEM diffraction patterns of Bi₂-xPbₓSr₂Co₂O₇ [(a): \(x=0\) and (b): 0.4]. The hexagonal diffraction patterns from the CoO₂ layer and the square diffraction patterns from the Bi₂Sr₂O₅ layer are clearly observed. The b-axis length of the hexagonal CoO₂ layer \(b_{H}\) is independent of Pb concentration within the resolution limit, and is about 2.8 Å. From these two diffraction pattern images, we notice that the distance between the (020\(_H\)) and (040\(_{RS}\)) spot of \(x=0\) is narrower than that of \(x=0.4\), indicating the enhancement of misfitting. Another remarkable difference between TEM diffraction patterns is the satellite diffraction patterns along the oblique direction from \(d_{RS}\)-axis and \(b_{RS}\)-axis seen in the \(x=0\) sample. This satellite diffraction patterns are due to the modulation structure, which is also observed in high-T \(_C\) Cu oxide Bi₂Sr₂CaCu₂O₈\(_{δ+}\). The modulation structure was confirmed by the Laue transmission photographs with incident x-ray beam perpendicular to the \(ab\)-plane. Figure 2(c) and (d) show the Laue patterns of \(x=0\) and 0.4 samples respectively. A two-fold symmetry Laue pattern, where an axis of symmetry is tilted about 45 from \(a_{RS}\)- or \(b_{RS}\)-axis, can be observed, while the Laue pattern of \(x=0.4\) sample shows a four-fold symmetry along the \(a_{RS}\)- and \(b_{RS}\)-axes. This two-fold symmetry Laue pattern agrees well with that of superconducting compound Bi-2212, which have modulation structure [12].

![Figure 2](image)

**Figure 2.** TEM diffraction patterns of Bi₂-xPbₓSr₂Co₂O₇ [(a): \(x=0\) and (b): 0.4]. Laue transmission photographs with incident x-ray beam perpendicular to the \(ab\)-plane [(c): \(x=0\) and (d): 0.4]

Figure 3(a) shows the temperature dependence of the a- and b-axis (of the rock-salt layer) resistivities for various Pb concentrations. The magnitude of the resistivity decreases with increasing Pb concentration, indicating carrier doping by the substitution of divalent Pb for trivalent Bi. These resistivities are normalized at room temperature in Fig. 3(b). The slope of the resistivity increases with Pb concentration, which also indicates the carrier doping. In a rough estimation of the carriers based on the nominal composition, 20% (\(x=0.4\)) substitution of Pb introduces 0.2 hole per Co atoms. The decrease of the resistivity from \(x=0\) to 0.4 at room temperature seems to be smaller than expected from the above estimation. Actually, reported Hall coefficient does not change very much, which indicate that less than 0.05 hole per Co atoms is introduced by 20% substitution of Pb [13]. On the other hand, Pb substitution strongly suppresses the upturn behavior at low temperatures. These results suggest that the Pb substitution works not only as carrier doping, but also changes the electronic structure of the CoO₂ layer.

Figures 4(a)-(c) show the temperature dependence of the thermopower measured along the a- and b-axis directions. The magnitude of the thermopower of both directions increases with increasing Pb concentration from \(x=0\) to 0.4. In conventional thermoelectric materials, the thermopower and the resistivity depend on the carrier concentration, and the thermopower is expected to decrease when the resistivity decreases with increasing carrier concentration. Thus the increase in the thermopower is considered to be due to the discontinuous shrink of the rock-salt b-axis length, which overcomes the decrease of the thermopower by doping. The chemical pressure induced by the misfit structure enhances the
Figures 3. (a) Temperature dependence of the $a$- and $b$-axis resistivities. (b) They are normalized at room temperature.

The thermopower as is seen in the pressure dependence of the thermopower in the Ce-based compound [14].

On the other hand, the thermopower decreases with further Pb doping from $x=0.4$ to 0.6. Since the crystal structure is nearly unchanged, observed decrease in the thermopower and resistivity is attributed to the increase of the carrier concentration.

Next we will discuss the in-plane anisotropy in the resistivity ($\rho_b/\rho_a$) and thermopower ($S_b/S_a$). Figures 5(a) and (b) show the temperature dependence of $\rho_b/\rho_a$ and $S_b/S_a$, respectively. For all Pb concentrations, $\rho_b/\rho_a$ decreases with decreasing temperature near the room temperature, while it increase rapidly below 80 K, which indicate that $\rho_a$ is more conductive than $\rho_b$ in low temperature. $\rho_b/\rho_a$ of $x=0.4$ is as large as 2.5 at 4.5 K, while $\rho_b/\rho_a$ of $x=0.6$ decreases due to the suppression of the upturn along the $b$-axis. We have previously proposed that the large in-plane anisotropy is come from the anisotropic pseudogap formation. If the misfit structure lowers the crystal symmetry of the CoO$_2$ layer to induce the spin-density-wave-like state, the anisotropic pseudogap would be open [9]. Actually, $S_b/S_a$ and $\rho_b/\rho_a$ are considered to be dominated by the density of states, because the magnitude and the temperature dependence of $S_b/S_a$ and $\rho_b/\rho_a$ roughly correspond to each other.

On the other hand, the increase in the anisotropy at low temperature in high-$T_c$ Cu oxide have been discussed in relation to the stripe order [10]. Since the triangular CoO$_2$ layer itself no in-plane anisotropy, large in-plane anisotropy in the resistivity suggests the self-organization of the electronic system as high-$T_c$ Cu oxide.

By looking carefully, one can find that $\rho_b/\rho_a$ of $x=0$ is somewhat smaller than $S_b/S_a$. We attribute this to the modulation structure, which works as an anisotropic scattering center in Bi-2212 [15]. The anisotropy would be averaged by the modulation structure, whose direction is tilted by 45 degrees from the $a$- and $b$-axis direction.

Figure 4. Temperature dependence of the thermopower along $a$- and $b$-axes.

Figure 5. In plane anisotropy in the resistivity ($\rho_b/\rho_a$) and thermopower ($S_b/S_a$).
Conclusions
We have successfully grown the large single crystal of Bi$_2$-,Pb$_x$Sr$_2$Co$_2$O$_y$ by TSFZ method and measured the in-plane anisotropy in the resistivity and thermopower. From the structural analysis, significant change in the b$_{ab}$-axis length of the rock salt Bi$_2$Sr$_2$O$_3$ layer has observed between x=0 and 0.4, which causes the enhancement of the misfit. The 15% increase in thermopower is due to the increase of the chemical pressure, as seen in the Ce-based compounds. These results indicate the thermoelectric properties can be controlled by modulating the misfit. There is a large in-plane anisotropy in the resistivity and thermopower. The anisotropic pseudogap formation at low temperatures would make the resistivity nonmetallic and the thermopower larger along the a$_{ab}$-direction. Another scenario of the large in-plane anisotropy is a charge stripe as seen in the lightly doped high-T$_c$ superconductor. In the case of the resistivity for x=0, the modulation structure along the oblique direction from the a$_{ab}$- and b$_{ab}$-axes averages the anisotropy.

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