Thermoelectric Properties of $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$ Thin Films and Single Crystals

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Abstract

$\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_9$ exhibits a misfit-layered structure with good thermoelectric properties. We have investigated the thermoelectric properties of $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$ in both thin-film and single-crystal forms. Among thin films grown at different temperatures, we find that both the in-plane thermoelectric power (S_{ab}) and electrical resistivity (ρ_{ab}) vary in an opposite trend, i.e., S_{ab} is high when ρ_{ab} is small. This results in large power factor ($S_{ab}^2/\rho_{ab} \sim 5.5 \mu\text{W}/\text{K}^2 \text{ cm}$ for the film grown at 700°C), comparable to that for whiskers. For single crystals, the electrical resistivity shows metallic behavior in a large temperature range, but has higher magnitude than that of films grown at 675°C and 700°C . The annealing of single crystals under Ar atmosphere leads to even higher resistivity while S_{ab} is improved. We discuss the thermoelectric performance of this material considering both oxygen concentration and phase purity.

I. INTRODUCTION

Layered cobaltates have attracted great attention for both their fundamental aspects and applications. The common feature is that they consist of CoO_2 layers formed by edge-sharing CoO_6 octahedra. Depending on the interlayer spacer, they may exhibit superconductivity¹, ionic conduction², or good thermoelectric properties³⁻⁷. The latter is particularly unexpected because traditional thermoelectric materials are usually semiconductors involving heavy-mass elements such as Bi_2Te_3 ⁸. Layered cobaltates like Na_xCoO_2 and $\text{Ca}_3\text{Co}_4\text{O}_9$ contain much lighter elements, yet exhibit high thermoelectric power (S), low electrical resistivity (ρ), and low thermal conductivity (κ)^{4, 5, 9}. These are desired properties for thermoelectric applications, since the efficiency is determined by the figure of merit $ZT = S^2/(\rho\kappa)$. It is expected that the layered structure is responsible for low ρ and low κ , but not obvious why S is high. Possible mechanisms for large S in cobaltates include (1) the unique electronic structure with the Fermi energy level located at the edge of a narrow band¹⁰, and (2) the low spin state of Co^{3+} ⁷. According to band calculations¹⁰, $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_9$ is expected to exhibit higher S than that of Na_xCoO_2 and $\text{Ca}_3\text{Co}_4\text{O}_9$. This prediction is in contradiction with the second scenario, as stoichiometric $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_9$ contains Co^{4+} only. Thus, the origin of its good thermoelectric properties needs to be further explored.

$\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_9$ exhibits the monoclinic symmetry consisting of two subsystems: a $\text{Bi}_2\text{Sr}_2\text{O}_4$ rock-salt (RS) layer and a CoO_2 (CO) layer^{11, 12}. As depicted in Fig. 1(a), these layers are stacked alternately along the c axis with identical lattice parameters a and c , and angle β , but different lattice parameter b (b_{RS} for the $\text{Bi}_2\text{Sr}_2\text{O}_4$ and b_{CO} for CoO_2). As b_{RS} and b_{CO} are incommensurate¹³, $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_9$ is characterized as having a misfit structure similar to $\text{Ca}_3\text{Co}_4\text{O}_9$. In addition to the enhancement of phonon scattering for low κ , the highly-strained RS layer may give rise to strong electron-phonon coupling¹⁴. One way to tune this strain is to use different alkaline-earth (AE) metals: the ratio of $b_{\text{RS}}/b_{\text{CO}}$ increases with increasing the ionic size of AE, and becomes commensurate when $\text{AE} = \text{Ba}$ with $b_{\text{RS}}/b_{\text{CO}} = 2$ ¹⁵. Depositing material on misfitting substrates would be another effective way to tune the strain. So far, $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$ has been grown on LaAlO_3 and fused silica substrates^{16, 17}. Although films grown on fused silica are more epitaxial than that on LaAlO_3 , the thermoelectric properties are superior in the latter

case ¹⁶, suggesting that strain plays a role. In this Letter, we report the thermoelectric properties of $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$ thin films and single crystals. Comparing our data with others obtained from literature, we discuss the thermoelectric performance of $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$ in various forms.

II. EXPERIMENTAL TECHNIQUES

The $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$ thin films were deposited on (0001) sapphire ($\alpha\text{-Al}_2\text{O}_3$ with the hexagonal structure $a = 4.76 \text{ \AA}$ and $c = 12.99 \text{ \AA}$) substrates by the pulsed laser deposition (PLD) technique under various growth conditions to find the optimal growth condition. The films reported here are $1000 \text{ \AA}$ thick which were grown in oxygen pressure of 0.03 Torr at growth temperatures $T_g = 625, 650, 675, 700, \text{ and } 750 \text{ }^\circ\text{C}$, respectively. The $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$ single crystals were grown using the floating-zone technique. The initial chemicals of Bi_2O_3 , SrCO_3 and Co_3O_4 in stoichiometric molar ratio of 1: 2: $2/3$ were well mixed and sintered at $900 \text{ }^\circ\text{C}$ for 24 hours to form polycrystalline $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$. After grinding, the reactants were pressed under hydrostatic pressure into two rods with 8 mm diameter and a length of $\sim 10 \text{ cm}$ for the feed rod and of $\sim 3 \text{ cm}$ for the seed rod. Crystals were grown at a speed of 1.5 mm/h and rotation speed of 20 rpm in air. The resultant crystals have easy cleavage planes perpendicular to the growth direction.

The structures of films and crystals were investigated by x-ray diffraction (XRD) using Cu $K\alpha$ radiation (wavelength = $1.5406 \text{ \AA}$) at room temperature. The structures of films were also studied using a VG603 scanning transmission electron microscope (STEM) operated at 300 keV to obtain high angle annular dark field (also known as Z-contrast) images. The characterizations of the thermoelectric properties of films and crystals were performed in a Physical Property Measurement System (PPMS) using the four-probe method. Film samples were cut in $10 \text{ mm} \times 3 \text{ mm} \times 1 \text{ mm}$, and single crystal samples were cut into $10 \text{ mm} \times 3 \text{ mm} \times 3 \text{ mm}$. For single crystals, the thermopower and thermal conductivity of samples were simultaneously measured along the ab plane. To avoid Joule heating, the electrical resistivity and Hall coefficient were measured separately, along the ab plane as well.

III. RESULTS AND DISCUSSIONS

Figs. 1b and 1c show the XRD patterns of films grown under 0.03 Torr oxygen at 750 °C and 625 °C, respectively. In both cases, the major peaks correspond to the $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_9$ phase along the c axis, as indicated by dots. For the film grown at 750 °C (Fig. 1b), there are signals from the Al_2O_3 substrate (indicated by *) and unknown phases (marked by triangles). XRD intensity from unknown phases decreases with decreasing growth temperature, becoming almost undetectable for the film grown at 625 °C. This suggests that the phase of epitaxial films is better optimized if grown at lower temperatures due most probably to the highly volatile Bi.

Fig. 1: (a) Schematic crystallographic structure of $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_9$; (b-c) XRD patterns of the $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$ films grown at 750 °C (b) and 625 °C (c), respectively; (d) STEM image of film grown at 750 °C; (e) XRD pattern of a grounded $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$ crystal.

To understand how impurity phases developed during the growth, films were investigated using STEM. Figure 1d shows a Z-contrast image of the film grown at 750 °C. Two features are worth noting: (1) the film is mostly single crystalline with well-stacked sequence Bi-O, Sr-O and Co-O along the c axis, corresponding to the $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_9$ phase (see Fig. 1a); and (2) intermediate layers are formed due to missing planes, yielding different lattice sizes in the first couple of layers next to the substrate. The latter could attribute to the unknown peaks in the XRD pattern (see Fig. 1b). These unidentified phases appear to involve the similar layered structures as $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_9$, but with different unit cell size and order. Figure 1e shows the XRD pattern from powder by crushing single crystals. All peaks can be indexed with the $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_9$ phase with $a = 4.99 \text{ \AA}$, $b = 5.43 \text{ \AA}$, and $c = 14.89 \text{ \AA}$. The lattice parameter c for films is expected to be the same, as all c -axis peak positions are the same in both films and single crystals (Figs. 1b, c and e).

Fig. 2a displays the temperature dependence of the in-plane electrical resistivity (ρ_{ab}) of $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$ thin films between 100 and 400 K. Note the resistivity increases with decreasing temperature for all our films. Such semiconducting behavior is quite different from that grown on LaAlO_3 or fused silica which show metallic behavior above $\sim 100 \text{ K}$ ^{16, 17}. Further, ρ_{ab} for our films initially decreases with decreasing growth temperature then increases after reaching the minimum for the film grown at 700 °C. Such non-monotonic behavior between resistivity and T_g is unexpected. As these films were deposited under the same atmosphere, the major difference between them would be the reduction of unknown phases with decreasing T_g , which would lead to the monotonic change of ρ_{ab} with T_g . It is possible that T_g impacts the oxygen content y . With the fixed T_g but varied oxygen pressure, electrical resistivity becomes higher than that presented in Fig. 2a. We thus consider that the growth conditions for the film grown at 700 °C are optimal when using Al_2O_3 substrates. Note that ρ_{ab} for the film grown at 700 °C is (1) almost temperature independent, and (2) lower than that obtained from the film grown on LaAlO_3 ^{16, 17}. This suggests that strain due to substrates plays a role in the physical properties of $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$ films.

Fig. 2b shows the temperature dependence of S_{ab} of the thin films between 100 and 400 K. In this temperature range, S_{ab} is positive for all samples, implying hole-dominant electrical transport. For each film, S_{ab} increases with increasing temperature at low temperatures, then

tends to saturate above 250 K, except for the film grown at 750 °C. Similar to the behavior seen in electrical resistivity, S_{ab} depends non-monotonically on the growth temperature. For example, with decreasing T_g , $S_{ab}(T = 300 \text{ K})$ initially increases then decreases after reaching the maximum for the sample at $T_g = 675 \text{ °C}$. The maximum thermopower ($\sim 120 \mu\text{V/K}$) obtained at 400 K is comparable to the reported value for the film grown on LaAlO_3 ^{16, 17}.

Fig. 2: Temperature dependence of electrical resistivity (a) and thermopower (b) of the films grown at 625, 650, 675, 700, 750 °C, respectively; (c-d) are temperature dependence of resistivity (c) and thermopower (d) of the as-grown and Ar-annealed single crystal samples.

Fig. 2c depicts the temperature dependence of ρ_{ab} for a $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$ single crystal between 2 and 400 K. For the as-grown single crystal, ρ_{ab} decreases with decreasing temperature down to $\sim 20 \text{ K}$ with a small upturn at lower temperatures. While theoretical calculations suggest that $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_9$ has a metallic ground state^{10, 18}, the low-temperature upturn is attributed to the charge ordering of Co^{3+} and Co^{4+} ¹¹ or pseudogap formation^{16, 19}. In the former case, oxygen deficiency would result in the presence of mixed Co^{3+} and Co^{4+} . From

this point of view, our as-grown single crystals are closer to stoichiometry. To confirm, the as-grown single crystal was annealed at 500 °C in Ar atmosphere for 50 hours. Such annealing is expected to reduce oxygen, forming $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_{9-\delta}$ with $y = 9 - \delta < 9$. As shown in Fig. 2c, the resistivity of the Ar-annealed single crystal exhibits non-metallic character ($d\rho/dT < 0$), similar to that seen in our films (Fig. 2a) and the film on silica¹⁶. Thus, it is conceivable that the upturn of electrical resistivity is related to oxygen deficiency. Among all films, the one grown at 700 °C is also close to stoichiometry.

Fig. 2d shows the temperature dependence of S_{ab} for both the as-grown and Ar-annealed $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$ single crystals. Note that S_{ab} increases with increasing temperature without saturation in both cases, which is different from that in films (Fig. 2b). Furthermore, S_{ab} is enhanced upon the annealing in Ar atmosphere, reaching $\sim 135 \mu\text{V/K}$ at 400 K. The increase of both ρ_{ab} (Fig. 2c) and S_{ab} (Fig. 2d) suggests that Ar annealing reduces carrier concentration in single crystals. According to previous studies^{13, 20}, the conduction carriers in $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_9$ are hole dominant. Annealing in Ar atmosphere likely reduces oxygen content, thus reducing hole concentration.

To confirm the carrier type, Hall effect measurements are performed, which reveal positive Hall coefficient R_H (not shown). This result is consistent with the positive S_{ab} shown in Fig. 2, indicating that the conduction carriers are indeed hole dominant. Fig. 3a shows the temperature dependence of carrier concentration n deduced from $n = \frac{1}{R_H e}$ (e is electrical charge). For two films (grown at 650 and 750 °C) and annealed crystals, n tends to decrease with decreasing temperature, consistent with the semiconducting behavior revealed by electrical resistivity. In contrast, n for the as-grown single crystal increases with decreasing temperature due to the metallic conduction. At room temperature, all samples have carrier concentration in the order of 10^{19} cm^{-3} . To understand the relationship between carrier concentration and electrical conduction, we plot room-temperature ρ versus n in Fig. 3b. Note that the film grown at 675 °C has higher carrier concentration and lower electrical resistivity compared with the one grown at 650 °C. While crystals show a similar trend, their resistivities are higher than that of films with the same carrier concentrations. It is likely that the resistivity for our single crystals is overestimated due to error introduced by geometrical configurations, as a previous report gave

much smaller resistivity values for single crystals with similar $\rho(T)$ profile ²¹. Nevertheless, Annealing under Ar atmosphere results in reduced carried concentration, suggesting partial removal of oxygen in the system.

Fig. 3: (a) Temperature dependence of carrier concentration n deduced from Hall coefficient for as-grown and annealed crystals, and films grown at 650 °C, and 675 °C; (b) Electrical resistivity versus carrier concentration for selected samples at $T = 300$ K; (c) The growth temperature dependence of thermopower and electrical resistivity of films at 300 K; (d) The power factor of films (empty triangulars) and crystals (empty square for as grown single crystal and filled square for crystal annealed in Ar) compared to reported results from samples with various forms (represented by filled triangulars: whiskers ^{22, 23}, films ^{16, 17}, single crystals ²⁴, and polycrystal ²⁵).

Thermopower in layered cobaltates (Na_xCoO_2 ⁴, $\text{Ca}_3\text{Co}_4\text{O}_9$ ⁵) is usually explained by Heike's formula $S = -\frac{k_B}{e} \ln\left(\frac{g_3}{g_4} \frac{x}{1-x}\right)$, where g_3 and g_4 are the numbers of possible states of Co^{3+} and Co^{4+} ions, respectively, and x is the concentration of Co^{4+} ions ⁷. In the simplest case, the optimal thermopower is expected to reach $2k_B/e = 170$ μV/K (k_B is the Boltzmann constant) with

optimal $n \sim 10^{19} \text{ C/cm}^3$ ²⁶. While n for as-grown single crystals and films grown at 675 °C is at the optimal level, their thermopower is in the order of 110 $\mu\text{V/K}$ (at 300 K), slightly lower than the expected value. Interestingly, annealing our $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$ single crystals in Ar results in the enhanced thermopower (Fig. 2d) but increased resistivity (Fig. 2c) and reduced carrier concentration (Fig. 3a). This is a typical trend seen in bulk materials. The variation of ρ_{ab} and S_{ab} observed in films seems different from that in single crystals. Compared to single crystals, a film deposited on a LaAlO_3 substrate reveals lower ρ_{ab} and higher S_{ab} , while a film deposited on silica has higher ρ_{ab} and lower S_{ab} ¹⁶. For comparison, we plot both $\rho_{ab}(T = 300 \text{ K})$ and $S_{ab}(T = 300 \text{ K})$ for our films in Fig. 3c. Remarkably, upon the variation of the growth temperature, $\rho_{ab}(T = 300 \text{ K})$ and $S_{ab}(T = 300 \text{ K})$ exhibit opposite trend, i.e., a film with higher S_{ab} has lower ρ_{ab} and vice versa. We recall that there is similar trend in Na_xCoO_2 , in which thermopower increases but electrical resistivity decreases with increasing x in the range of $0.55 \leq x \leq 0.75$ ²⁷. Obviously, the combined high S_{ab} and low ρ_{ab} would lead to high power factor, S_{ab}^2/ρ_{ab} , which is in favor of thermoelectric performance.

As pointed out by Ierasaki²⁶, although thermopower has been discussed with the Heikes formula for transition-metal oxides, little is known on how the electrical resistivity is described in the same condition. For the system with non-metallic conduction, the power factor is expected to be independent on the carrier concentration²⁶. This is apparently not true for $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$ films as shown in Fig. 3d: S_{ab}^2/ρ_{ab} for $T_g = 700 \text{ }^\circ\text{C}$ is more than 5 times larger than that for the film grown at 625 °C. For comparison, Fig. 3d also shows the power factor obtained from $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$ in other forms including polycrystals, single crystals, and whiskers. It can be seen that S_{ab}^2/ρ_{ab} depends not only on the sample in each form but also on sample confinement. Overall, lower dimensionality produces a higher power factor, consistent with the theoretical prediction²⁸.

With the reduced dimensionality, the thermal conductivity (κ) of a system is usually reduced because of enhanced phonon scattering²⁸. When a material is prepared in forms other than bulk 3D structure, it becomes more technically challenging to accurately measure κ . But κ obtained from single crystals may be considered as the upper bound for thin films. Fig. 4a shows the temperature dependence of in-plane thermal conductivity κ_{ab} of $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$ single crystals before and after annealing between 100 and 400 K. Both increase with increasing temperature,

and are almost coincident with each other. Similar magnitude and temperature dependence of thermal conductivity was reported previously for the same system^{29, 30}. This was explained by considering optical phonon contribution in $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$ ³⁰. The fact that κ_{ab} is unchanged for both as-grown and annealed samples indicates that the electronic contribution to κ_{ab} is negligible (we estimate room-temperature electronic contribution about 0.067 W/K·m for the as-grown sample and 0.041 W/K·m for the annealed sample using the Wiedemann-Franz Law). It is worth noting that the magnitude of κ_{ab} is much lower than that for $\text{Na}_{0.5}\text{CoO}_2$ compound⁹, which can be attributed to its misfit crystal structure and thick block layer ($\text{Bi}_2\text{Sr}_2\text{O}_4$)²⁹. Therefore, we estimate the ZT for single crystals and films using κ_{ab} presented in Fig. 4a. Fig. 4b displays the temperature dependence of ZT , which increases with increasing temperature. At room temperature, the ZT of the as-grown crystal is about 0.02. After annealing, ZT decreases due to poor electrical resistivity. The film has significantly higher ZT than crystals, reaching 0.12 at 400 K.

Fig. 4: Temperature dependence of thermal conductivity (a) and figure of merit ZT (b) for as-grown and annealed single crystals, and the film grown at 700 °C.

IV. CONCLUSIONS

In summary, we have investigated the thermoelectric properties of $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$ in both the thin-film and single-crystal forms. While all films were grown under the same oxygen atmosphere, their thermopower, resistivity, and carrier concentration vary non-monotonically with growth temperature. This indicates that property change cannot be simply due to impurity

phase seen in films grown at high temperatures. Remarkably, the thermopower and electrical resistivity of these films vary with growth temperature in opposite trend: thermopower increases while electrical resistivity decreases. This provides great opportunity to tune the power factor that reaches the maximum (much higher than that for single crystals) in the film grown at 700 °C. Based on the thermoelectric property measurements on single crystals, oxygen vacancy is one factor that impacts the thermoelectric performance in this material. Overall, samples under confined dimensionality show better thermoelectric properties. Although all films display non-metallic behavior, the high thermopower, low thermal conductivity, and metallic conduction seen in single crystals strongly suggest that it is possible to improve the thermoelectric performance of $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_9$ with optimized processing conditions.

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