High temperature thermoelectric properties of highly *c*-axis oriented $Bi_2Sr_2Co_2O_y$ thin films fabricated by pulsed laser deposition*

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High-temperature thermoelectric transport property measurements have been performed on the highly *c*-axis oriented $Bi_2Sr_2Co_2O_y$ thin films prepared by pulsed laser deposition on $LaAlO_3$ (001). Both the electric resistivity ρ and the seebeck coefficient S of the film exhibit an increasing trend with the temperature from 300 K–1000 K and reach up to 4.8 m·Ω · cm and 202 μV/K at 980 K, resulting in a power factor of 0.85 mW/mK which are comparable to those of the single crystalline samples. A small polaron hopping conduction can be responsible for the conduction mechanism of the film at high temperature. The results demonstrate that the $Bi_2Sr_2Co_2O_y$ thin film has potential application in high temperature thin film thermoelectric devices.

Keywords: high temperature thermoelectric properties, $Bi_2Sr_2Co_2O_y$ thin films, *c*-axis oriented, pulsed laser deposition

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1. Introduction

Thermoelectric (TE) materials can convert thermal energy directly into electricity, making them attractive for waste heat conversion applications. The performance of a TE material is evaluated by the dimensionless figure-of-merit $ZT = (S^2/\rho\kappa)T$, where S is the seebeck coefficient, ρ is the electric resistivity, κ is the thermal conductivity and T is the absolute temperature. Therefore, good TE materials should possess a large power factor ($PF = S^2\rho$) and a low thermal conductivity.

Oxide materials are promising for TE applications because of their good thermal stability, lack of sensitivity to the air and non-toxicity.[1−3] Especially, layered cobalt oxides have attracted great interest since the discovery of good thermoelectric performance in Na_xCoO_2.[4] Among various layered cobalt oxide studied, $Bi_2Sr_2Co_2O_y$ (abbreviated as Bi-222) is considered to be a promising high temperature TE candidate material due to its good thermoelectric performance and excellent chemical stability in air at high temperature. Extensive studies have been performed on the high temperature TE properties of the Bi-222 whiskers and bulks.[5−9] The highest ZT values of about 1.1 and 0.26 have been achieved at about 1000 K for the single crystalline whiskers and the high-pressure sintered Pb-doped polycrystalline bulks respectively.[5,7] For many thermoelectric devices for localized heating or cooling, thin films are required. High quality Bi-222 thin films have been obtained on various single crystal substrates and their low temperature TE properties have been investigated.[10−12] However, so far there has been no report on the high temperature TE properties of a thin film sample.

In this paper, we report on the high temperature TE properties of the *c*-axis oriented Bi-222 thin films fabricated by pulsed laser deposition (PLD). The film shows a relatively high power factor of 0.85 mW/mK^2 at 980 K, suggesting that the Bi-222 film has a great potential application in the high temperature TE film devices.

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2. Experiments

The Bi-222 thin films were fabricated on the $LaAlO_3$ (001) single crystal substrates by a PLD method. An excimer laser with the wavelength of 308 nm was used for ablation of the ceramic Bi-222 target sintered by the traditional solid state reaction method. The laser energy density and the repetition rate were of 1.5 J/cm^2–2 J/cm^2 and 3 Hz. An oxygen pressure of 40 Pa was maintained during the film growth at substrate temperatures of 680 °C. After the deposition, the films were rapidly cooled to 500 °C in the oxygen with the pressure being slightly lower than 1 atm (1 atm = 10^5 Pa) and annealed at this temperature for about 30 min. The thickness of the films was measured by a Dektak150. The crystal structure of the films was measured using X-ray diffraction (XRD) with CuKα radiation. The four-probe electrical resistivity and the seebeck coefficient were measured in air using a commercial equipment (Linseis, LSR-3) over the temperature range of 300 K–1000 K.

3. Results and discussion

We measured the XRD θ–2θ scans of the PLD-grown Bi-222 thin film on $LaAlO_3$ (001) in the temperature range of 300 K–650 K and no structure transition was observed during this measured temperature range. Figure 1(a) presents a typical XRD θ–2θ pattern of the film recorded at 300 K. It shows that the film is pure phase and highly c-axis oriented. Rocking curve measurement is made by doing a θ scan at a fixed 2θ angle, the width of which is inversely proportional to the dislocation density in the film and is therefore used as a gauge of the quality of the film. The rocking curve of Bi-222 (0012) peak in Fig. 1(b) shows a full width at half maximum (FWHM) of only 0.1°, confirming the high crystalline quality of the PLD-grown film.

The high temperature TE properties of the PLD-grown Bi-222 films are characterized by the temperature dependence of in-plane resistivity ρ, seebeck coefficient S and power factor $S^2\rho$ in the temperature range of 300 K–1000 K. We measured several film samples and all these samples showed similar ρ–T and S–T behaviors. Figure 2(a) is the ρ–T curve of a 155-nm thick film. The resistivity shows an increasing trend with the temperature, suggesting a metallic-like conduction behavior ($\mathrm{d}\rho/\mathrm{d}T > 0$). At 980 K, the film has a resistivity of about 4.8 m$\Omega \cdot$ cm, which is comparable to the resistivity obtained from Bi-222

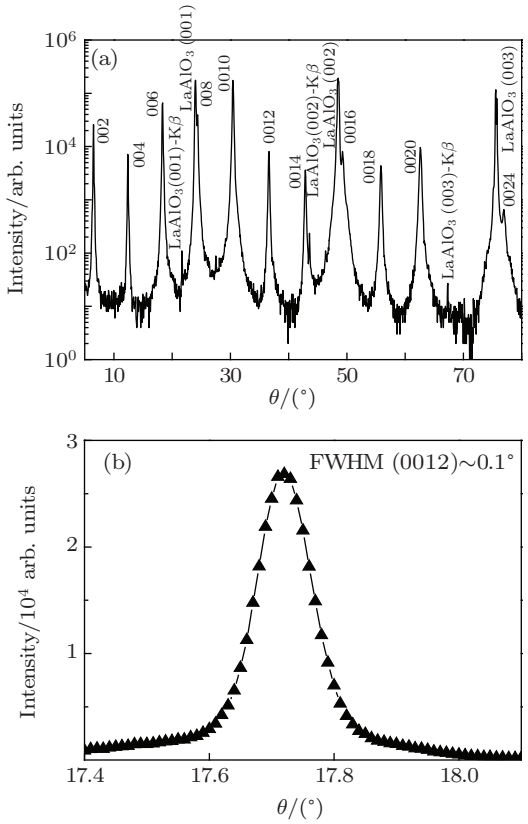


Fig. 1. (a) The XRD θ–2θ pattern and (b) the rocking curve of the PLD-grown Bi-222 thin film on (001) $LaAlO_3$ substrate.

single crystalline whiskers[5,6] and much lower than those obtained from the polycrystalline samples.[7–9] In addition, an obvious change in the resistivity is observed at about 530 K. Similar behavior in the ρ–T curves were observed in $Ca_3Co_4O_9$ at temperature of about 420 K, and they were attributed to the Co^{3+} and Co^{4+} spin state transitions from a low spin state at room temperature to an intermediate spin state at the measured temperature.[13,14] A similar mechanism is suggested to be responsible for the observed change in the electric properties of Bi-222 film at about 530 K since XRD measurements demonstrate that no observable structural transition occurs in Bi-222 at this temperature.

To further understand the high temperature conduction mechanism of the Bi-222 film, a small polaron hopping conduction (SPHC) model was used to fit the resistivity data in the high temperature region of $T > 550$ K. According to the SPHC mechanism, the temperature dependence of resistivity can be generally expressed as

$$\frac{1}{\rho} = \sigma \sim \frac{1}{T} \exp\left(\frac{-E_\mathrm{a}}{\kappa_\mathrm{B} T}\right),$$

where σ is the electric conductivity, k_B is the Boltzmann constant, E_a is the activation energy, and T is

the absolute temperature. The plot of $\ln(\sigma T)$ versus $1000/T$ of the film shows a straight line curve above approximately 550 K, shown in the inset of Fig. 2(a), indicating the hopping conduction behavior of the Bi-222 film at high temperature.

Figure 2(b) plots the variation of the seebeck coefficient S with the temperature of the same film from 300 K to 1000 K. The positive S over the measured temperature range indicates the hole carrier conduction mechanism. The value of S increases with the temperature and reaches up to 202 μV/K at 980 K. The exact origin of such a large seebeck coefficient with metallic-like conduction in the Bi-222 phase has not yet been so clear and it is possibly induced by the spin entropy as in Na_xCoO_2.[15]

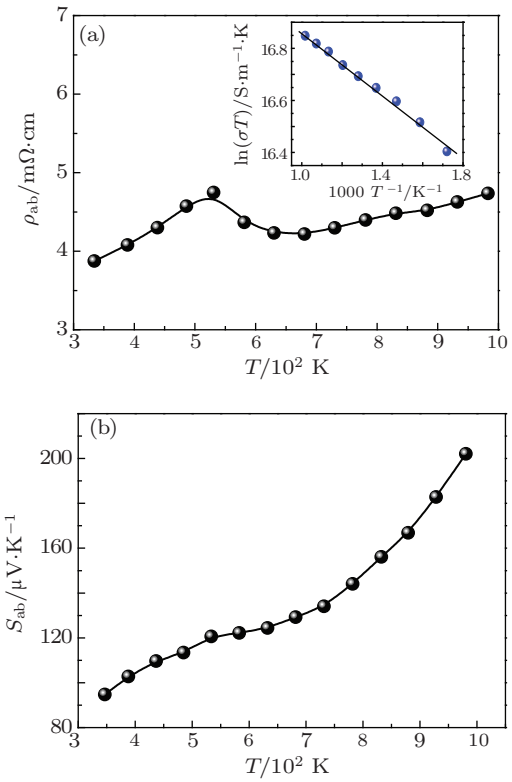


Fig. 2. (colour online) The temperature-dependent thermoelectric properties of the PLD-grown Bi-222 thin film: (a) in-plane resistivity ρ_{ab} and (b) in-plane seebeck coefficient S_{ab}. The inset of Fig. 2(a) is the plot of $\ln(\sigma T)$ versus $1/T$ in the high temperature region of $T > 550$ K.

Figure 3 displays the dependence of the power factor on temperature of the PLD grown Bi-222 film. The power factor of the film at 980 K is 0.85 mW/mK^2, which is comparable to the value of 0.90 mW/mK^2 for the Ca and Pb-doped Bi-222 single crystalline whiskers and much higher than that of the polycrystalline bulks (about 0.1 mW/mK^2–0.26 mW/mK^2).[6–8] The corresponding thermal conductivity κ of the PLD-grown film has not yet been obtained due to the difficulty in measuring κ for a few hundred nm thickness thin film sample. However, we can expect that the film has a low thermal conductivity due to the scattering at the film surface and film/substrate interface.[16] Therefore, a relatively high ZT of these films is expected at high temperature.

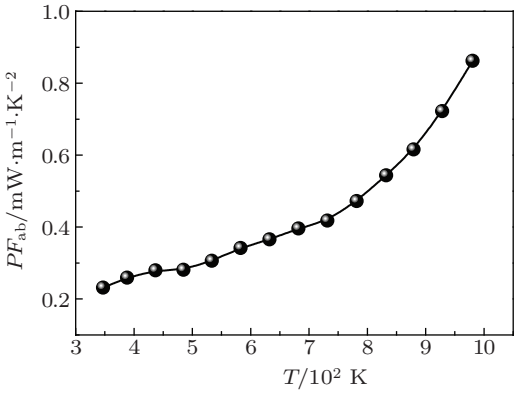


Fig. 3. The in-plane power factor PF_{ab} versus temperature curve for the PLD-grown Bi-222 thin film.

4. Conclusion

In conclusion, we have investigated the high temperature thermoelectric properties of the highly c-axis oriented Bi-222 thin films fabricated by PLD. The films show a high power factor of about 0.85 mW/mK^2 at 980 K, which is comparable to that of the single crystal whisker and much better than those of the polycrystalline bulks. Relatively high ZT can be expected in the Bi-222 thin films considering the fact that the scattering at film surface and film/substrate interface can reduce the thermal conductivity. The results demonstrate that the c-axis oriented Bi-222 thin film has a great potential application in the high-temperature thin film thermoelectric devices.

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