学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Study on Thermal Stability of Thermoelectric $Ba_{1/3}CoO_2$ Thin Films
（熱電 $Ba_{1/3}CoO_2$ 薄膜の熱安定性に関する研究 ）

Thermoelectric materials enable direct conversion between heat and electricity and are therefore attractive for waste heat recovery and solid-state energy conversion. The performance of thermoelectric materials is commonly evaluated by the dimensionless figure of merit *ZT*, defined as $ZT = S^2 \sigma T/\kappa$, where *S* is the thermopower, σ is the electrical conductivity, κ is the thermal conductivity, and T is the absolute temperature [1]. Higher *ZT* values correspond to more efficient thermoelectric energy conversion.

Metal chalcogenide thermoelectric materials such as PbTe [2], SnSe [3], and Bi_2Te_3 [4] have achieved record-high thermoelectric performance with *ZT* values exceeding 2 and have been extensively investigated. However, these materials often contain toxic or scarce elements and exhibit limited chemical and thermal stability in oxidizing or high-temperature environments. Such drawbacks significantly restrict their long-term reliability, particularly under operation in air or under sustained thermal gradients. In contrast, oxide-based thermoelectric materials are environmentally benign and exhibit excellent chemical and thermal stability under oxidizing conditions. Among them, layered cobalt oxides with A_xCoO_2-type structures (A = Na, Ca, Sr, and Ba) have attracted considerable interest as p-type thermoelectric materials due to their unusually large thermopower combined with relatively high electrical conductivity, originating from strongly correlated Co 3d electrons in the CoO_2 layers [5].

Among layered cobalt oxides, epitaxial $Ba_{1/3}CoO_2$ (BCO) thin films exhibit outstanding thermoelectric performance, with an in-plane *ZT* of approximately 0.11 at room temperature [6] and up to 0.55 at 600 °C [7] in ambient air. These values are among the highest reported for oxide thermoelectrics and are comparable to those of commercial PbTe and SiGe-based thermoelectric materials. Such characteristics make BCO a promising candidate for high-temperature thermoelectric applications.

Despite these outstanding properties, scaling up BCO for practical applications remains a significant challenge. Epitaxial BCO thin films typically have a thickness of approximately 150 nm and are grown as heterostructures on insulating substrates such as Al_2O_3 or yttria-stabilized zirconia (YSZ), whose thickness is on the order of 0.5 mm. Consequently, although the intrinsic thermoelectric properties of the BCO films are excellent, the overall thermoelectric performance of the entire sample is severely suppressed by the dominant thermal and electrical contributions of the substrates. As a result, thermoelectric properties evaluated in epitaxial thin-film geometries do not directly reflect the performance achievable at the device level.

Moreover, from the perspective of practical thermoelectric device implementation, epitaxial thin films inherently suffer from structural and processing limitations, since most thermoelectric generators are fabricated using bulk or ceramic materials. Previous attempts to fabricate bulk BCO ceramics have resulted in significantly degraded thermoelectric performance. For example, Liu et al. reported *ZT* values of only 0.014 at room temperature and 0.15 at 520 °C, which are much lower than those of epitaxial BCO thin films [8]. However, the origin of this pronounced discrepancy between thin-film and bulk thermoelectric performance has not yet been fully clarified.

To advance BCO as a practical thermoelectric material, it is therefore essential to verify the reproducibility of its thermoelectric properties in single-crystalline BCO that is free from substrate effects, and to elucidate the mechanisms responsible for the performance degradation observed in bulk materials. Fundamental studies that

clarify the relationship between structural evolution and thermoelectric transport during scale-up processes are critically required.

In this thesis, I fabricated freestanding single-crystalline BCO sheets and carefully verified that their thermoelectric properties are comparable to those of epitaxial thin films. In addition, by annealing BCO thin films in air up to 1000 ^{o}C, I clearly elucidated the origin of thermoelectric performance degradation and the thermal instability at high temperatures. This thesis is composed of the following chapters:

In Chapter 1, the fundamental principles of thermoelectrics, the development of thermoelectric materials, and the characteristics of layered cobalt oxides are introduced.

In Chapter 2, the experimental methods used for thin-film growth, structural characterization, and thermoelectric property measurements are described.

In Chapter 3, I reported the fabrication of freestanding BCO single-crystalline sheets using a water-soluble sacrificial layer method and systematically investigated their thermoelectric properties. By removing the substrate, I directly evaluated the intrinsic electrical and thermal transport properties of BCO without substrate-induced suppression. The freestanding single-crystalline sheets retained high electrical conductivity and large thermopower, demonstrating that the excellent thermoelectric performance of epitaxial BCO thin films originates from intrinsic material properties.

In Chapter 4, I reported a systematic investigation of the high-temperature decomposition behavior of BCO and its impact on electron transport and thermoelectric performance. Epitaxial BCO thin films were annealed in air over a wide temperature range from 100 ^{o}C to 1000 ^{o}C, and the resulting structural evolution and transport properties were analyzed. I demonstrated that BCO undergoes phase decomposition above approximately 700 ^{o}C, forming $BaCoO_3$, $BaCoO_{2.6}$, and Co_3O_4. This structural decomposition induces a transition in the dominant electron transport mechanism from metallic conduction to percolation conduction, leading to a pronounced degradation of electrical conductivity and thermoelectric performance during high-temperature annealing.

In Chapter 5 the present study is summarized.

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