$Ba_{1/3}CoO_2$エピタキシャル薄膜の熱電特性の温度依存性

Temperature Dependence of Thermoelectric Properties of $Ba_{1/3}CoO_2$ Epitaxial Films

北大院情報 [1], 北大電子研 [2] ○(M2)呉 礼奥 [1], 張 雨橋 [2], 張 習 [2], ジョヘジュン [2], 太田裕道 [2]

IST-Hokkaido U. [1], RIES-Hokkaido U. [2], °L. Wu[1], Y. Zhang[2], X. Zhang[2], H.J. Cho[2], Hiromichi Ohta[2]

E-mail: go1reioku@gmail.com

Among many kinds of conducting oxides, layered cobalt oxides such as $Na_{3/4}CoO_2$ and $Ca_3Co_4O_9$ have been extensively studied as p-type thermoelectric materials. Based on our own hypothesis[1] that the thermal conductivity of layered cobalt oxides can be reduced by the ion exchange treatment without suppressing the power factor, recently, we found that $Ba_{1/3}CoO_2$ shows rather high ZT of 0.11 at room temperature[2]. Here we report the thermoelectric properties of $Ba_{1/3}CoO_2$ epitaxial films at elevated temperatures. Although rather high thermoelectric figure of merit, ZT (~1.2 at 800 K for Na_xCoO_2 single crystal[3]) of layered cobalt oxides have been reported thus far, reliable ZT (~0.3 at 700 °C[4]) is quite small as compared to that of chalcogenide such as PbTe. Such inconsistency is often seen in the literatures published in high impact factor journals[5], probably due to the instability of conducting oxides at elevated temperatures. Therefore, we firstly studied the stability of $Ba_{1/3}CoO_2$ epitaxial films at elevated temperatures. Then, we measured the thermoelectric properties of the $Ba_{1/3}CoO_2$ epitaxial films at elevated temperatures.

$Ba_{1/3}CoO_2$ epitaxial films were prepared as following. Firstly, $Na_{3/4}CoO_2$ epitaxial films were prepared by the R-SPE method[6]. Then, Na^+ ions were exchanged with Ba^{2+} ions by the ion exchange treatment. Resistivity, thermopower, and thermal conductivity of the $Ba_{1/3}CoO_2$ epitaxial films were measured by dc four probe method, steady state method, and TDTR method, respectively.

We firstly measured the XRD patterns, resistivity, and thermopower of the $Ba_{1/3}CoO_2$ films at room temperature after the films were annealed at several temperatures in air. As the results, the limitation temperature of the $Ba_{1/3}CoO_2$ films was ~600 °C, which is higher than that of $Na_{3/4}CoO_2$ (~350 °C) (**FIG.**). Next, we measured the temperature dependence of resistivity, thermopower and thermal conductivity of the $Ba_{1/3}CoO_2$ films. Above room temperature, the power factor of the $Ba_{1/3}CoO_2$ films was almost constant (~1 mW m^{-1} K^{-2}), which is similar to $Na_{3/4}CoO_2$ films. Thermal conductivity of $Ba_{1/3}CoO_2$ films exhibited decreasing tendency from ~3 W m^{-1} K^{-1} at room temperature to ~1.7 W m^{-1} K^{-1} at 300 °C. As the result, the ZT increased from ~0.11 at room temperature to ~0.33 at 300 °C. Unfortunately, we could not measure the thermal conductivity above 300 °C due to that oxidation of Mo transducer film occurs at high temperature in air. We would update the thermoelectric properties of $Ba_{1/3}CoO_2$ films by using appropriate metal transducer film in future.

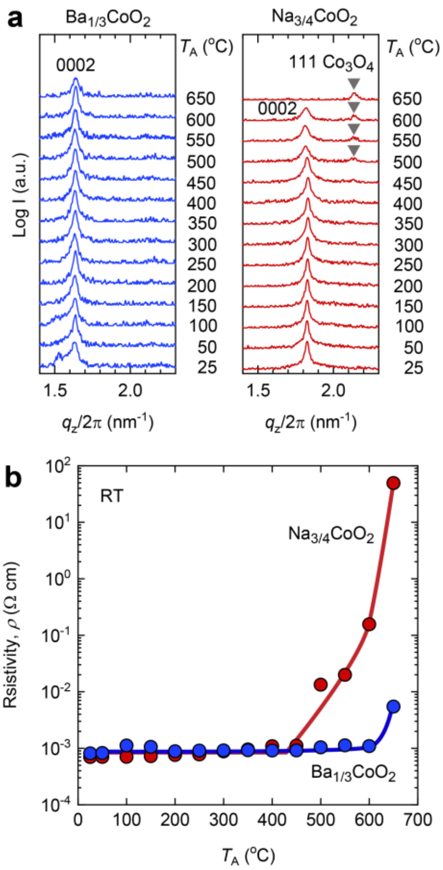

FIG. Changes in (**a**) the XRD patterns and (**b**) room temperature resistivities of $Ba_{1/3}CoO_2$ and $Na_{3/4}CoO_2$ epitaxial films after annealing at elevated temperatures.

[1] H.J. Cho *et al.*, *Adv. Mater. Interfaces* **7**, 1901816 (2019).
[2] Y. Takashima *et al.*, *J. Mater. Chem. A* **9**, 274 (2020).
[3] *eg*. K. Fujita *et al.*, *Jpn. J. Appl. Phys.* **40**, 4644 (2001).
[4] H. Ohta *et al.*, *Inorg. Chem.* **47**, 8429 (2008).
[5] *eg*. M. Acharya *et al.*, *Nano Energy* **84**, 105905 (2021).
[6] H. Ohta *et al.*, *Cryst. Growth Des.* **5**, 25 (2005).