High Temperature PTC Thermistor Using Ba Cobaltite

Kazuya Kinoshita,* Hajime Kusaba, Go Sakai,[†] Kengo Shimanoe,[†] Norio Miura,[††] and Noboru Yamazoe[†]
Department of Molecular and Material Sciences, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Fukuoka 816-8580
[†]*Department of Materials Science, Faculty of Engineering Sciences, Kyushu University, Fukuoka 816-8580*
[††]*Advanced Science and Technology Center for Cooperative Research, Kyushu University, Fukuoka 816-8580*

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It was found that partially Fe-substituted Ba cobaltite, $BaCo_{0.7}Fe_{0.3}O_{3-\delta}$, shows sharp PTC behavior at temperature above 850 °C. As revealed by XRD measurements, the PTC behavior is accompanied by phase transformation between hexagonal perovskite structure (low temperature) and cubic one (high temperature).

The resistor whose resistivity increases abruptly on raising temperature is called a positive temperature coefficient (PTC) thermistor. This peculiar electronic property can be applied as a heating element with temperature-selfcontrolling capability. The most well known PTC thermistors are based on $BaTiO_3$ and its derivatives which show resistance variations of 3 to 7 orders of magnitude due to the ferroelectric to paraelectric phase transformation involved.[1] The PTC thermistors of this group have been well exploited and those which exhibit PTC behavior at various temperatures in the range of −30 – +400 °C are now available. However little has been known about the PTC thermistor working at high temperature above 500 °C. In the course of our study on the relation between oxygen permeable properties and phase transformation for cobaltite-based perovskite-type oxide,[2] we found that partially Fe-substituted Ba cobaltite, $BaCo_{0.7}Fe_{0.3}O_{3-\delta}$, shows sharp PTC behavior at temperature above 850 °C, as described below.

$BaCo_{0.7}Fe_{0.3}O_{3-\delta}$ (A) and a partially Yb-substituted derivative of it, $Yb_{0.05}Ba_{0.95}Co_{0.7}Fe_{0.3}O_{3-\delta}$ (B), were prepared from Co acetate and nitrates of the other constituent metals. Aqueous solutions dissolving these salts to the desired compositions were evaporated to dryness at 350 °C before calcination in air at 850 °C for 5 h. The resulting powder samples were compacted into a disk, 20 mm in diameter and 2 mm thick under a pressure of 100 MPa, and sintered by calcining at 1100 °C in air for 5 h. Then the disk was cut into a rod (2 mm × 2 mm × 18 mm) for the measurement of electrical conductivity in air by means of a four-probe (Pt) dc technique. Under the constant current (10 mA) flow, dc voltage drop between the inner two probes was measured, while the rod specimens were heated or cooled at a rate of 5 °C min^{-1}. Figure 1 shows the electrical resistivities of both specimens (A and B) as a function of temperature. The resistivity of specimen A decreased sharply at about 850 °C on cooling, while it increased sharply at about 900 °C on heating. The PTC behavior is thus obvious, although hysteresis is significant under the present experimental conditions. Specimen B, on the other hand, showed a gradual resistivity change as a normal semiconductor over the tested temperature range. The structural change was pursued for powder samples by using a high temperature X-ray diffractometer. In these measurements, XRD patterns were recorded at an interval of 50 °C; each recording took 40 min and 20 min was needed for the next temperature to be settled. As shown in Figure 2, sample A underwent phase transformation from cubic structure to hexagonal on cooling at temperature between 950 and 850 °C, indicating that this transformation is responsible for the PTC behavior just mentioned. It follows also that the hysteresis of phase transformation is responsible for that in PTC behavior. In contrast, sample B was confirmed to keep cubic structure down to room temperature. As mentioned above, $BaCo_{0.7}Fe_{0.3}O_{3-\delta}$ shows PTC behavior at high temperature. Like the case of $BaTiO_3$-based thermistors, the PTC behavior is accompanied by phase transformation, although its mechanism is yet to be elucidated. For this particular compound, the magnitude of resistivity change on going from low temperature phase (about 0.04 Ωcm) to high temperature phase (0.14 Ωcm) is still far smaller than the case of $BaTiO_3$-based thermistors. Further material exploitations would possibly lead to a greater resistivity change as well as to a

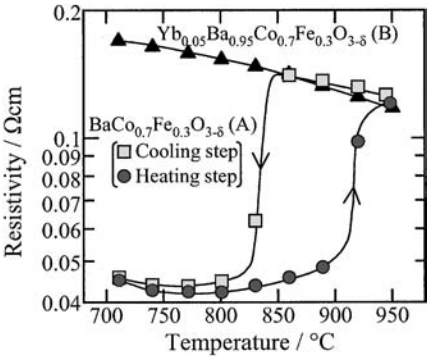

Figure 1. Resistivity of $Yb_{0.05}Ba_{0.95}Co_{0.7}Fe_{0.3}O_{3-\delta}$ and $BaCo_{0.7}Fe_{0.3}O_{3-\delta}$ as a function of temperature.

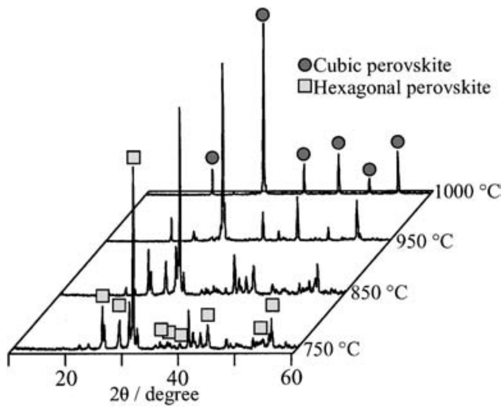

Figure 2. High temperature XRD patterns of $BaCo_{0.7}Fe_{0.3}O_{3-\delta}$ (cooling step).

variation in the phase transformation (PTC) temperature, which are important for establishing a new class of PTC thermistors using Ba cobaltites.

References and Notes

1 E. Andrich, *Electronic Applications*, **26**, 26 (1965).
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