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A hot spot in a $GdBa_2Cu_3O_{7-\delta}$ ceramic rod with a core of Gd_2BaCuO_5 fabricated by dip coating

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A $GdBa_2Cu_3O_{7-\delta}$ ceramic rod with a core of Gd_2BaCuO_5 was prepared by dip coating. A hot spot appeared in the rod when a voltage exceeding a certain value was applied at room temperature. Moreover, the hot spot was broken into two when the voltage was increased further. A mechanism for the appearance of the double hot spots is discussed from the viewpoint of the change of resistance in the hot spot.

Key words: dip coating, complex oxide, oxygen sensor, hot spot.

Introduction

$LnBa_2Cu_3O_{7-\delta}$ (Ln: rare earth element), which are well known as high-Tc superconductors, are nonstoichiometric oxides. The oxygen deficiency δ increases with an increase in temperature above 400 °C [1]. The carrier density decreases with increasing δ which results in a steep increase of the resistivity [2-4]. In other words, the material shows a positive temperature coefficient of resistivity (PTCR).

Our group reported a phenomenon that a local area of a $GdBa_2Cu_3O_{7-\delta}$ (Gd-123) ceramic rod glows orange once a voltage exceeding a certain value is applied to the rod at room temperature [5]. The glowing area was named a hot spot. The current through the rod decreases abruptly when the hot spot appears, and remains constant with increasing voltage [6-8]. The current after the appearance of the hot spot depends on the oxygen partial pressure in the ambient atmosphere, which acts as an oxygen sensor without the need for any heating system [6, 9].

To enable the practical use of the hot spot oxygen sensor, the durability is important. The Gd-123 rod tends to be molten and broken by the sustained presence of the hot spot, because the temperature of the hot spot (900 °C) is close to melting point of Gd-123 (1020 °C) [7, 10]. In previous papers, we demonstrated that the durability of the sensor was improved using a Gd-123 rod with dispersed Gd_2BaCuO_5 (Gd-211) because the melting point of Gd-211 (1200 °C) was higher than that of Gd-123 [11]. In the present study, the hot spot phenomenon of a Gd-123 ceramic rod with a core of Gd-211 was investigated.

Experimental

A ceramic rod of Gd-123 with a core of Gd-211 was prepared by dip coating. Gd-123 powder and a Gd-211 rod were prepared by conventional solid-state reaction as follows.

For the preparation of the Gd-211 rod, starting powders of Gd_2O_3 (Soekawa Chemical, 99.99% purity), $BaCO_3$ (Soekawa Chemical, 99.99% purity) and CuO (Soekawa Chemical, 99.9% purity) were weighed in a ratio of Gd : Ba : Cu = 2 : 1 : 1 and mixed for 1 h in ethanol using a planetary ball mill (Fritsch, Pulverissete-7). The mixture was calcined at 850 °C for 10 h in air and ground into powder. The Gd-211 powder was uniaxially pressed at 10 MPa and cold-isostatic-pressed at 200 MPa. The green body was sintered at 1200 °C for 10 h in air. The sintered body was cut into a rod (0.65 × 0.65 mm^2 × 60 mm).

For the preparation of the Gd-123 powder, Gd_2O_3, $BaCO_3$ and CuO were weighed in a ratio of Gd : Ba : Cu = 1 : 2 : 3 and mixed for 1 h in ethanol using a planetary ball mill. The mixture was calcined at 900 °C for 10 h in air and ground into powder. The powder was sintered at 910 °C for 10 h in air and ground into powder again.

The Gd-123 powder, 1-pentanol and polyoxyethylene alkyl (C_{14}~C_{18}) amine were weighed in the mass ratio of 100 : 83 : 17 and mixed to obtain a slurry. The Gd-211 rod was coated with the slurry using a dip coater (EINTESLA, MD-0408) and sintered at 900 °C for 10 h in air.

The surface morphology of the resultant rod were observed using an optical microscope (Keyence, VH-7000). Phases for the sample obtained were analyzed using an X-ray diffractometer (XRD; Rigaku, Multi Flex 2 kW). The microstructures were observed using a scanning electron microscope (SEM; JEOL, JSM-5510). The elemental mappings were obtained using energy dispersive X-ray spectrometer (EDS; JEOL, JED-2201). Atomic ratios of Gd, Ba and Cu were determined using EDS with atomic number absorption fluorescence (ZAF) correction. The electrical characteristics were measured by a four-probe method with the distance between voltage electrodes being 26 mm.

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Results and Discussion

Fig. 1 shows SEM images and EDS elemental maps of Gd for the fractured surface of the sample. In the SEM image, a core and a coat were confirmed (a). In the elemental maps, the white area indicates a high concentration of Gd (b). The Gd was observed to concentrate higher in the core than the coat, indicating that the core was Gd-211 and the coat was Gd-123. A boundary between the Gd-123 coat and the Gd-211 core located in a white square area in (a) and (b) were enlarged and shown in (c) and (d), respectively. The density of the Gd-211 core was higher than that of the Gd-123 coat (c), reflecting the high sintering temperature of 1200°C for Gd-211 core.

Fig. 2 shows the current-voltage characteristic of the rod. The voltage was increased at a rate of 0.5 V/30 s. During the measurement of the characteristic, photographs of the rod were taken as shown in Fig. 3. When a dc voltage was changed from 11.1 V to 15.4 V, the current decreased and a hot spot appeared. The spot size increased with increasing voltage. When the voltage was changed from 20.1 V to 21.6 V, the current decreased abruptly and the hot spot was broken into two (Fig. 3(a) to (b)). After that, the current remained almost constant with increasing voltage. When a voltage of 50.5 V was applied, the rod was molten and fractured at the hot spot of the negative electrode side.

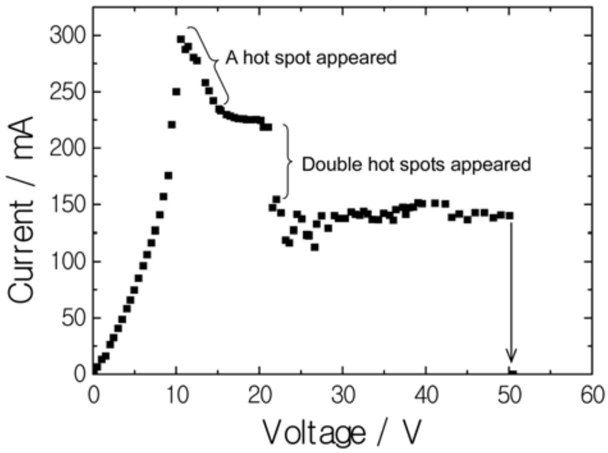

Fig. 2. Current-voltage characteristic of the Gd-123 ceramic rod with a core of Gd-211. The arrow indicates the fracture of the rod caused by melting.

Previously no report has been given of two hot spots appearing in a rod at the same time. The appearance of the double hot spots is a new phenomenon which appears in the Gd-123 ceramic rod with a core of Gd-211.

Optical micrographs of the sample before and after the appearance of the double hot spots are shown in Fig. 4. It was observed that the smooth surface (a) changed to rough

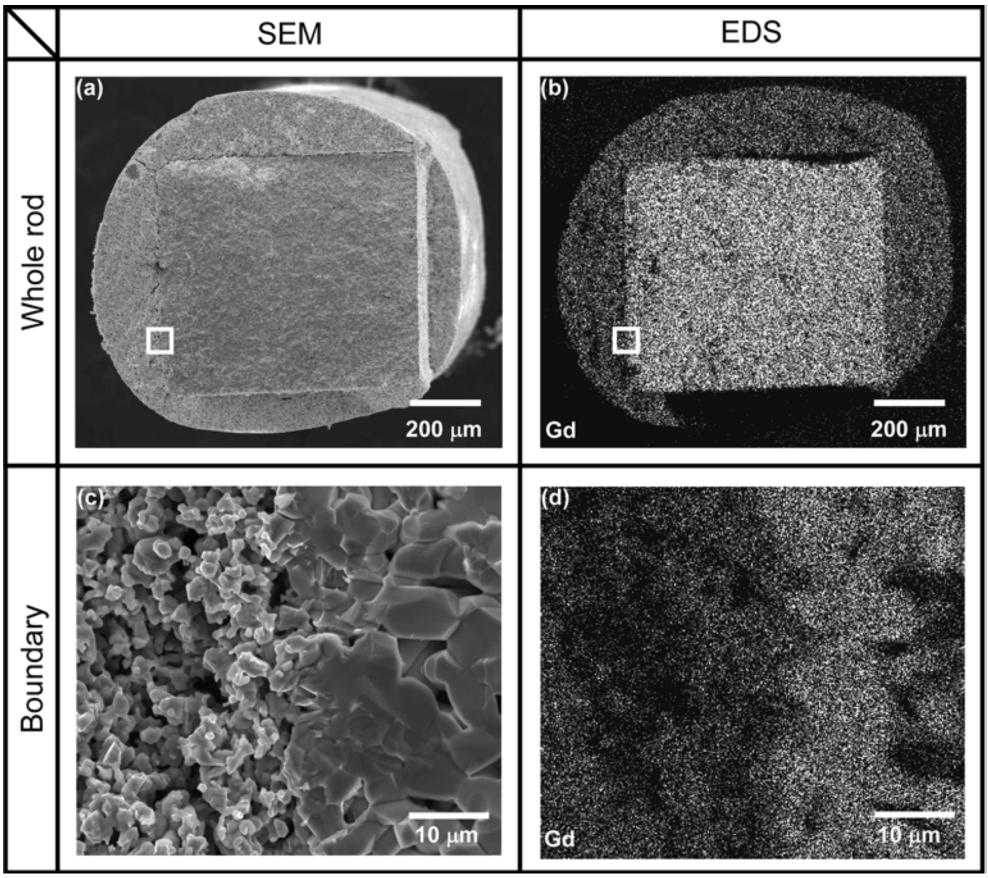

Fig. 1. SEM images and EDS elemental maps of Gd for the fractured surface of the Gd-123 ceramic rod with a core of Gd-211. (a): SEM image of the whole rod. (b): EDS elemental map of the whole rod. (c): The enlargement of white area in (a). (d): The enlargement of white area in (b).

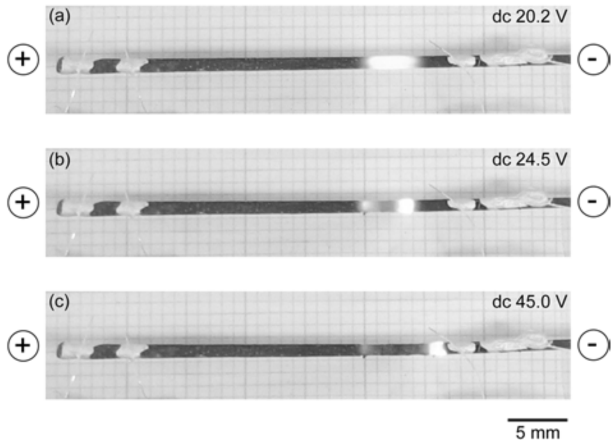

Fig. 3. Photographs of the Gd-123 ceramic rod with a core of Gd-211 at (a) 20.2 V, (b) 24.5 V and (c) 45.0 V. The presence of double hot spots in the rod was confirmed in (b) and (c).

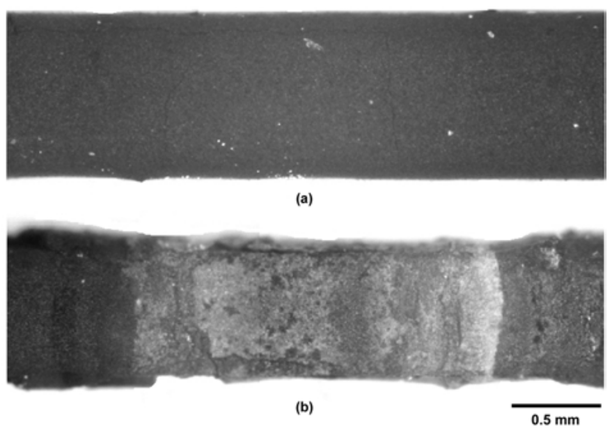

Fig. 4. Optical micrographs of the surface morphology. (a) Before the appearance of the double hot spot. (b) After the appearance of the double hot spots. The smooth surface changed to rough. The diameter of the rod was decreased with the appearance of the double hot spots.

(b). The diameter of the rod was decreased with the appearance of the double hot spots.

Fig. 5 shows XRD patterns before and after the appearance of the double hot spots. All the peaks before the appearance were assigned only to Gd-123. On the other hand, the peaks after the appearance could be assigned to Gd-123 and Gd-211. It was reported that Gd-123 single phase was changed to liquid phase and Gd-211 at 1020 °C [10]. From the results, it is considered that the Gd-123 coat in the hot spot was changed to liquid phase and Gd-211.

Table 1 shows atomic ratios of Gd, Ba and Cu for the cross section of the Gd-211 core before and after the appearance of the double hot spots. The atomic ratio of Gd : Ba : Cu was almost the same as 2 : 1 : 1 before the appearance. After the appearance the ratio of Ba and Cu increased. Therefore, the liquid generated by the partial melting of Gd-123 was proved to be absorbed into the Gd-211 core.

Fig. 6 shows temperature dependencies of the resistivity for Gd-123 and Gd-211. The temperature of the hot spot is approximately 900 °C [7]. The resistivity of Gd-211 was much higher than that of Gd-123 even at 900 °C. Therefore, the current was not considered to flow through the Gd-211 core.

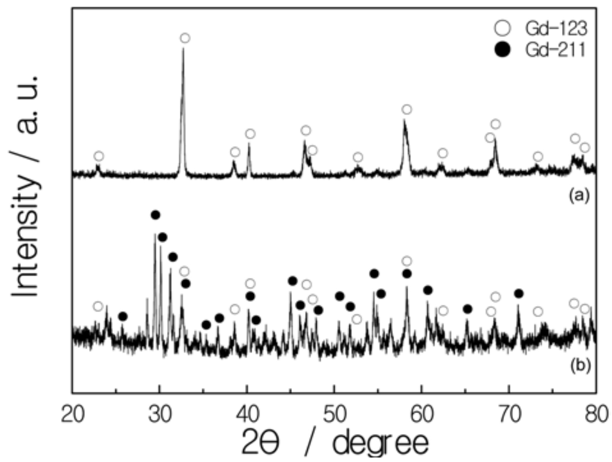

Fig. 5. XRD patterns of the rods (a) before and (b) after the appearance of the double hot spots.

Table 1. Atomic ratios in Gd-211 core before and after the appearance of the double hot spots. Atomic ratios were determined by EDS with ZAF correction

	Gd	Ba	Cu
Before the appearance of the double hot spot	2	0.89	0.90
After the appearance of the double hot spots	2	1.06	1.24

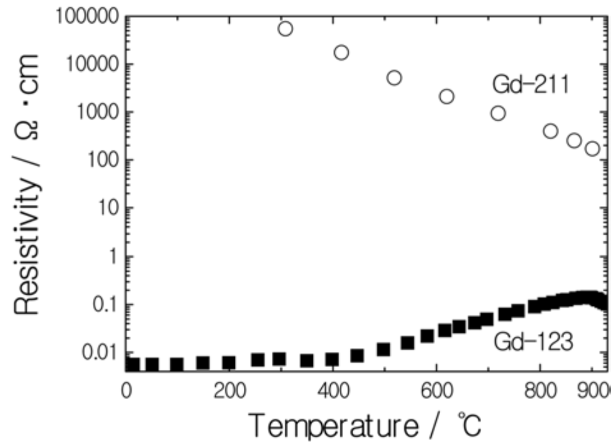

Fig. 6. Temperature dependencies of the resistivity for Gd-123 and Gd-211.

An appearance process for the double hot spots is assumed to be as follows (Fig. 7). A current mainly flows through the Gd-123 coat during the appearance of a hot spot (a). The center of the hot spot is supposed to be the hottest in the rod. Therefore, the Gd-123 at the center of the hot spot begins to melt at a certain voltage (b). The liquid generated by the partial melting of Gd-123 is absorbed into the Gd-211 core and a new current path appears (c). The fact that the hot spot was broken at the center reflects that the resistance of the center of the hot spot decreased and the temperature decreased, implying the formation of materials with a low resistivity in the Gd-211 core.

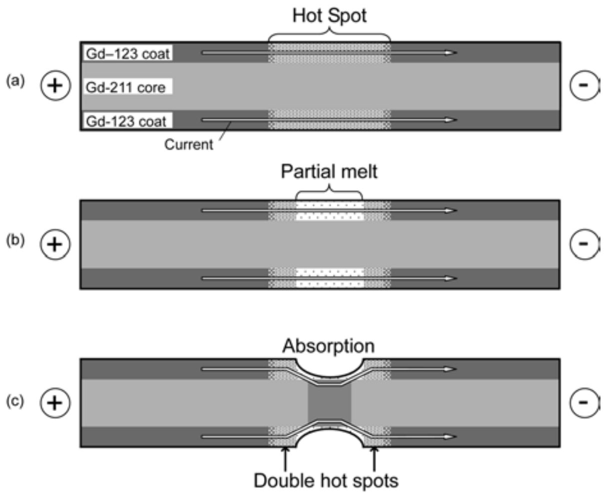

Fig. 7. Schematic explanation for the appearance process of the double hot spots. (a) The current mainly flows through the Gd-123 coat of the rod with the hot spot. (b) Gd-123 at the center of the hot spot begins to melt. (c) A new current path appears and the hot spot is broken into two.

Conclusions

A Gd-123 ceramic rod with a core of Gd-211 was prepared by dip coating. A hot spot appeared in the rod when a voltage exceeding a certain value was applied at room temperature. When the voltage was further increased the hot spot was broken into two, which is new phenomenon appearing in the Gd-123 ceramic rod with a core of Gd-211. A mechanism for the appearance of the double hot spots is related to the resistance change at the center of the hot spot. Liquid generated by the partial melting of Gd-123 was absorbed into the core of Gd-211 and decreased its resistance.

Acknowledgements

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