Characteristics of Oxygen Sensor Exploiting the Hot Spot in BaAl$_2$O$_4$-added GdBa$_2$Cu$_3$O$_{7-\delta}$ Composite Ceramic Rod

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GdBa$_2$Cu$_3$O$_{7-\delta}$-based composite ceramics with various BaAl$_2$O$_4$ contents were prepared by solid-state reaction. From the elemental maps of Al and Cu measured using an electron probe microanalyzer, BaAl$_2$O$_4$ grains were clearly distinguished from GdBa$_2$Cu$_3$O$_{7-\delta}$ grains. When a certain voltage was applied to the composite rod electric current decreased abruptly, and a hot spot appeared in the rod. After the appearance of the hot spot, the current remained constant with increasing voltage. The electric power required to melt the rod significantly increased upon adding BaAl$_2$O$_4$. The current after the appearance of the hot spot depended on the oxygen partial pressure in the ambient atmosphere. Compared with the GdBa$_2$Cu$_3$O$_{7-\delta}$ rod, the composite rod showed high durability for sensing applications even in high oxygen partial pressure. The results revealed that the BaAl$_2$O$_4$-added GdBa$_2$Cu$_3$O$_{7-\delta}$ composite ceramics is a promising material for use as an oxygen sensor exploiting the hot spot.

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1. Introduction

LnBa$_2$Cu$_3$O$_{7-\delta}$ (Ln: rare earth element), which is well known as a high-Te superconductor, is a typical nonstoichiometric oxide. Oxygen deficiency $\delta$ increases with increasing temperature above 400°C. The carrier density decreases with increasing $\delta$, which results in a steep increase of the resistivity. In other words, the material shows a positive temperature coefficient of resistivity (PTCR).

The present authors observed the phenomenon that a local area of a GdBa$_2$Cu$_3$O$_{7-\delta}$ ceramic rod glows orange once a voltage exceeding a certain value is applied to the rod at room temperature as shown in Fig. 1. The glowing area was named a hot spot. The hot spot moves to the negative electrode with the velocity of a few mm/min. The direction of movement can be reversed by switching the polarity. The appearance of the hot spot is considered to be related to the PTCR characteristics. The movement of the hot spot may be caused by the diffusion of oxide ions in the electric field over the hot spot.

The current through the rod decreases abruptly when the hot spot appears, and remains constant with increasing voltage. This is possible because the size of a hot spot with high resistivity increases linearly with increasing voltage. The rod with the hot spot can be used as a constant-current generator without any active component. The current after the appearance of the hot spot depends on the oxygen partial pressure in ambient atmosphere, which acts as an oxygen sensor without the need for any heating system. Under low oxygen partial pressure, the current vibrates in the form of damped sinusoidal oscillation, and the rod can be used as a low-frequency generator.

To enable the practical use of devices utilizing the hot spot, the durability of the rod should be considered. The temperature of the hot spot was about 900°C, which is almost the same as the sintering temperature of GdBa$_2$Cu$_3$O$_{7-\delta}$. The GdBa$_2$Cu$_3$O$_{7-\delta}$ rod tends to be molten and broken by a sustained presence of the hot spot. In the preceding paper on this issue, we demonstrated that a ceramic rod composed of GdBa$_2$Cu$_3$O$_{7-\delta}$ and BaAl$_2$O$_4$ withstood breakage. The improvement of the durability was considered to be related to the high stability of BaAl$_2$O$_4$ in the hot spot. Barium aluminate is stable up to high temperature (melting point, 1815°C), and known as a raw material for refractory cement, a ferroelectric material, and a fluorescent material. In the present study, GdBa$_2$Cu$_3$O$_{7-\delta}$-based composite ceramics with BaAl$_2$O$_4$ were prepared by solid-state reaction, and their characteristics as oxygen sensors compared with the GdBa$_2$Cu$_3$O$_{7-\delta}$ rod was investigated.

2. Experimental

The powders of GdBa$_2$Cu$_3$O$_{7-\delta}$ and BaAl$_2$O$_4$ were prepared by conventional solid-state reaction. The starting powders
Gd$_2$O$_3$, BaCO$_3$ and CuO (Soekawa Chemical, >99.9% purity) were weighed in the molar ratio of Gd : Ba : Cu = 1 : 2 : 3, mixed for 2 h in ethanol, dried and then sintered at 910°C for 10 h in air. The sintered body was then ground into powder to obtain the GdB$_2$Cu$_3$O$_7$-d powder. For the preparation of BaAl$_2$O$_4$ powder, the powders of BaCO$_3$ and Al$_2$O$_3$ (Soekawa Chemical, >99.9% purity) mixed in the ratio of Ba : Al = 1 : 2 were sintered at 1000°C in air for 10 h and ground into powder.

The GdB$_2$Cu$_3$O$_7$-d powder was mixed with 0–100 mol% BaAl$_2$O$_4$ powder, and sintered at 900°C for 5 h in air. The sintering temperature was set at low to obtain a porous sample in which the hot spot appears easily. The resultant samples were characterized by X-ray diffraction (XRD; Rigaku, RAD-2C), scanning electron microscopy (SEM; JEOL, JSM-5510) and energy dispersive X-ray spectroscopy (EDS; JEOL, JED-2201).

The samples were cut into a rod shape with a cross section of 0.65 mm × 0.65 mm. The electrical characteristics were measured by a four-probe method with the distance between voltage electrodes being 30 mm. Oxygen partial pressure (P$_{O_2}$) was controlled by changing the flow rates of N$_2$ and O$_2$.

3. Results and Discussion

Figure 2 shows SEM images and electron probe micro-analyzer (EPMA) maps of Cu and Al for the fractured surface of the sintered samples. In the elemental maps, the white area indicates a high concentration of the elements. The Cu and Al maps were considered to show the distributions of GdB$_2$Cu$_3$O$_7$-d and BaAl$_2$O$_4$, respectively, because XRD peaks attributed only to them were observed from the samples. The results show the samples have porous microstructure consisting of grains of both GdB$_2$Cu$_3$O$_7$-d and BaAl$_2$O$_4$.

Figure 3 shows the current-voltage characteristics of the GdB$_2$Cu$_3$O$_7$-d-based composite ceramic rods with various BaAl$_2$O$_4$ contents. The arrows indicate breaking of the rods caused by melting. For the rods with BaAl$_2$O$_4$ content higher than 70 mol%, the electrical resistance was too high to measure the characteristics. The current through the GdB$_2$Cu$_3$O$_7$-d rod increased linearly with increasing voltage, decreased abruptly at a certain voltage and then a hot spot appeared in the rod. With further increasing voltage, the current remained constant. With increasing BaAl$_2$O$_4$ content, the amount of current drop at the hot spot appearance decreased. The constant-current characteristic was observed in each rod after the appearance of the hot spot. It is clear that the electric resistance increased with increasing BaAl$_2$O$_4$ content. This result suggests that the current pass consisting of the conductive GdB$_2$Cu$_3$O$_7$-d grains is blocked with the insulating BaAl$_2$O$_4$ grains.

Figure 4 summarizes the minimum power required for the hot spot to appear and the maximum power before the rods break. With increasing BaAl$_2$O$_4$ content, the minimum power...
increased gradually. The maximum power increased significantly until the content increased to 30 mol%, and decreased when the content exceeded 50 mol%. From the results, the durability of the ceramic rod was expected to increase on adding BaAl₂O₄.

Figure 5 shows the oxygen-sensing characteristics for (a) a GdB₆.Cu₃O₇.₅₋₇.₅ rod and (b) a composite ceramic rod containing 30 mol% BaAl₂O₄. The applied voltages, 6 V for the GdB₆.Cu₃O₇.₅₋₇.₅ and 11 V for the composite, were set so that the size of hot spot would be 2 mm. The curves were measured in the order of increasing oxygen partial pressure in the variable P₀₂ region seen in Fig. 5. Compared to the characteristics of the composite rod, the current through the GdB₆.Cu₃O₇.₅₋₇.₅ rod was unstable in air. With higher P₀₂, the current tended to increase with time. For the composite rod, the current was stable even in O₂ atmosphere. It was reported that the hot spot showed an annealing effect, i.e., improvement of the electrical conductivity of the rod. The effect should be high in high P₀₂ because the temperature of the hot spot increases with increasing P₀₂. The increase of the current in high P₀₂ should be caused by the annealing effect of the hot spot.

Figure 6 shows the P₀₂ dependence of the current. The data were derived from Fig. 5. The GdB₆.Cu₃O₇.₅₋₇.₅ rod showed divergence from the dotted line in high P₀₂. The divergence might be caused by the annealing effect. For the composite rod, the relationship between the current and P₀₂ agreed well with the solid straight line shown in Fig. 6.

There is little difference between the slopes of the lines shown in Fig. 6, which reflects that the sensitivity to oxygen is mainly caused by GdB₆.Cu₃O₇.₅₋₇.₅. When the oxygen content (7−δ) of LnBa₆.Cu₃O₇.₅₋₇.₅ is higher than 6.2, the sample behaves like an oxygen excess (metal deficit) oxide. If the LnBa₆.Cu₃O₇.₅₋₇.₅ is kept at high temperature and the P₀₂ is raised, the sample absorbs oxygen that dissociates into holes and oxide ions. The overall reaction is expressed as

\[ O₂ = 2O₂^− + 4 h^+ \]  \hfill (1)

where \( O₂^− \) is an interstitial divalent oxide ion and \( h^+ \) is a hole. Therefore, the LnBa₆.Cu₃O₇.₅₋₇.₅ essentially has a \( p^- \) type conduction since the excess oxygen plays the role of acceptor. The mass action law for Eq. (1) is

\[ K = \frac{[O₂^−]^2 \cdot [h^+]^4}{[O₂]} \]  \hfill (2)

where \( K \) is the equilibrium constant, and \([O₂^−]\), \([h^+]\) and \([O₂]\) represent the concentrations of interstitial oxide ion, hole, and oxygen (=P₀₂), respectively. When the formation of defects represented by Eq. (1) is predominant, the insertion of the relation \( 2[O₂^−] = [h^+] \) into Eq. (2) yields

\[ [h^+] \propto P₀₂^{1/6}. \]  \hfill (3)

Since the conductivity \( \sigma \) is proportional to \([h^+]\), the \( \sigma \) is proportional to \( P₀₂^{1/6}. \) Though the temperature of the hot spot actually increases with \( P₀₂ \), a qualitative explanation can be made using Eq. (3).
Figure 7 shows the change of the current through the (a) GdBa₂Cu₃O₇₋ₓ and (b) composite rods under Pₒ₂ changing periodically between 100 and 1 kPa. The applied voltages were 9 V for the GdBa₂Cu₃O₇₋ₓ and 20 V for the composite. The currents were normalized by the initial values under Pₒ₂ = 100 kPa. The current through the GdBa₂Cu₃O₇₋ₓ rod increased with increasing cycle. After 50 min, the rod broke in two due to melting at the hot spot. On the other hand, the current through the composite showed a stable repetition.

The current through the rods with hot spots in O₂ atmosphere was measured and is shown in Fig. 8. The applied voltages were 6 V for GdBa₂Cu₃O₇₋ₓ and 11 V for the composite. The current through the GdBa₂Cu₃O₇₋ₓ rod increased irregularly. After 63 min, the rod broke in two due to the melting. The current through the composite rod increased gradually and the rod did not break even after 3000 min, reflecting a high durability in high Pₒ₂.

Figure 9 shows SEM images of the fractured surface of the samples after the sustained presence of the hot spot in O₂ atmosphere. After the voltage of 9 V was applied to the GdBa₂Cu₃O₇₋ₓ for 23 min (a), the grain size increased and the neck growth occurred at the junction between GdBa₂Cu₃O₇₋ₓ grains. The neck growth caused by the hot spot is considered to be the cause of the increase in the current. For the composite rod (b), a porous microstructure was still observed even after applying voltage of 11 V for 3000 min.

Local parts of the hot spot, particularly the boundaries between the GdBa₂Cu₃O₇₋ₓ grains, may become partially molten due to local deviation from the ideal composition. The presence of partial melt is considered to be the cause of the breaking at the hot spot. The microstructure shown in Fig. 9 suggests that BaAl₂O₄ maintained the microstructure even in O₂ atmosphere.

4. Conclusions

GdBa₂Cu₃O₇₋ₓ-based composite ceramic rods with various BaAl₂O₄ contents were prepared by conventional solid-state reaction. When a certain voltage was applied, a hot spot appeared in the rod. The current after the appearance of the hot spot depended on the oxygen partial pressure in ambient atmosphere. Compared to the GdBa₂Cu₃O₇₋ₓ ceramic rod, the composite rod had a high durability even in O₂ atmosphere. The results show that the composite ceramics of GdBa₂Cu₃O₇₋ₓ with BaAl₂O₄ is a promising material for use as an oxygen sensor exploiting the hot spot.

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![Fig. 7. Change of the current through the (a) GdBa₂Cu₃O₇₋ₓ and (b) GdBa₂Cu₃O₇₋ₓ-30 mol% BaAl₂O₄ rods under Pₒ₂ changing periodically between 100 and 1 kPa. The applied voltages were 9 V for the GdBa₂Cu₃O₇₋ₓ and 20 V for the composite. The currents were normalized by the initial values under Pₒ₂ = 100 kPa.](image)

![Fig. 8. Change of the current in O₂ atmosphere. The applied voltages were 6 V for GdBa₂Cu₃O₇₋ₓ and 11 V for GdBa₂Cu₃O₇₋ₓ-30 mol% BaAl₂O₄.](image)

![Fig. 9. SEM images of the fractured surface of (a) GdBa₂Cu₃O₇₋ₓ after applying 9 V for 23 min and (b) GdBa₂Cu₃O₇₋ₓ-30 mol% BaAl₂O₄ after applying 11 V for 3000 min in O₂ atmosphere.](image)
References