Absence of Distinctively High Grain-Boundary Impedance in Polycrystalline Cubic Bismuth Oxide

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ABSTRACT

In this work, we studied a fluorite structure oxides: Yttria stabilized zirconia, (YSZ); Gd doped CeO₂ (GDC); erbia stabilized Bi₂O₃ (ESB); Zr doped erbia stabilized Bi₂O₃ (ZESB); Ca doped erbia stabilized Bi₂O₃ (CESB) in the temperature range of 250 to 600°C using electrochemical impedance spectroscopy (EIS). As is well known, grain boundary blocking effect was observed in YSZ and GDC. However, there is no grain boundary effect on ESB, ZESB, and CESB. The Nyquist plots of these materials exhibit a single arc at low temperature. This means that there is no space charge effect on δ -Bi₂O₃. In addition, impedance data were analyzed by using the brick layer model. We indirectly demonstrate that grain boundary ionic conductivity is similar to or even higher than bulk ionic conductivity on cubic bismuth oxide.

Key words : Cubic bismuth oxide, Grain boundary blocking effect, Space charge, Electrochemical impedance spectroscopy

1. Introduction

δ -Bi₂O₃ is drawing much attention as the most well-known material among oxygen ionic conductors.¹⁻⁵⁾ The attention is due to the high ionic conductivity of δ -Bi₂O₃. The ionic conductivity of δ -Bi₂O₃ is higher than that of yttria stabilized zirconia (YSZ) (5×10^{-3} S/cm at 600°C), which is frequently used as an oxygen ionic conductor, by two orders of magnitude and is higher than that of gadolinium doped ceria (GDC) (2.5×10^{-2} S/cm at 600°C) by one order of magnitude.⁶⁻⁷⁾ The high ionic conductivity of δ -Bi₂O₃ is due to the oxygen vacancy concentration (25%) and the anion mobility in δ -Bi₂O₃ which values are higher than those of acceptor-doped ceria or acceptor-doped zirconia having the same fluorite-type structure (Fig. 1).⁸⁾ However, the overall ionic conductivity of actual polycrystals is determined by not only the bulk ionic conductivity but also the ionic conductivity of the grain boundaries. According to Guo,⁹⁾ in acceptor-doped zirconia and acceptor-doped ceria, which are materials having a fluorite-type structure like that of δ -Bi₂O₃, the ionic conductivity at the grain boundaries is several orders of magnitude lower than the bulk ionic conductivity, which is called the grain boundary blocking effect.¹⁰⁻¹⁴⁾ These two factors are often mentioned as the causes of the grain boundary blocking effect. First, grain boundary siliceous phases impede ionic conduction.¹³⁻¹⁴⁾ However, the grain boundary blocking effect is even found in high-purity materials.¹²⁻¹⁵⁾ This blocking nature can be accounted by the presence of a

space charge layer near the grain boundary core.^{12,16-17)} Many experiment results support a role of space charge. Lei used transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS) to determine an increase of oxygen vacancy and Y segregation at the grain boundary core of YSZ and also demonstrated that Gd segregation and oxygen vacancy were higher at the grain boundaries than in the bulk GDC.¹⁸⁾ Lee directly observed the Gd segregation and high concentration of oxygen vacancy near grain boundaries using scanning transmission electron microscopy-X-ray spectroscopy (STEM-EDS). In addition, in this work, Kelvin probe force microscopy (KFM) verified Grain boundary is positively charged and the potential difference between grain boundary and bulk. Moreover, the potential difference was equal to the calculated data from impedance analysis applying the Schottky barrier model.¹⁹⁾ However, same fluorite-type structure δ -Bi₂O₃ didn't show grain boundary effect.²⁰⁾ In this work we added an aliovalent dopant to δ -Bi₂O₃, as it was done in YSZ and GDC to know whether grain boundary effect shows or not. The difference of the ionic radius makes an elastic filed and it causes the segregation in the grain boundary.²¹⁾ So we selected a dopant which has a small ionic radius difference with Bi₂O₃ ($r[\text{Bi}^{3+}] = 1.17 \text{ \AA}$)²²⁾ to exclude the segregation effect as much as possible. A tetravalent donor ZrO₂ ($r[\text{Zr}^{4+}] = 0.84 \text{ \AA}$)²²⁾ and a divalent acceptor CaO ($r[\text{Ca}^{2+}] = 1.12 \text{ \AA}$)²²⁾ were doped to Bi₂O₃ to investigate the grain boundary blocking effect caused by the space charge layer. Using Kröger-Vink notation,²³⁾ we describe a doping Bi₂O₃ with donor and acceptor, as follows:

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Fig. 1. Crystal structure of (a) δ - Bi_2O_3 , (b) Gd doped ceria. Yttria stabilized zirconia (YSZ) has the same structure as (b).

Doping with the donor Zr was expected to lead to a positively charged space charge layer because of Zr_{Bi}' segregation at the grain boundary (Eq. 1a), while the doping with the acceptor Ca was expected to generate a negatively charged space charge layer because of the Ca_{Bi}' segregation at the grain boundary (Eq. 1b). Since δ - Bi_2O_3 is converted to α - Bi_2O_3 at 723°C ,²⁴ for stabilization at room temperature, we doped δ - Bi_2O_3 with 20 mol% Er. We call this erbia-stabilized bismuth (ESB), $\text{Bi}_{0.8}\text{Er}_{0.2}\text{O}_{1.5}$. In addition, 2 mol% Ca and 5 mol% Zr were doped into the ESB. Polycrystal 8 mol% Y doped ZrO_2 , single-crystal 8 mol% Y doped ZrO_2 , and 10 mol% Gd doped CeO_2 , which also have fluorite structure were used for comparison. In addition, we perform X-ray diffraction (XRD) analysis to identify synthesized materials. Microstructures of the samples were analyzed by scanning electron microscopy (SEM) to verify the absence of a secondary phase at the grain boundary. The ionic conductivity of the bulk and the grain boundaries is measured with the electrochemical impedance spectroscopy.

2. Experimental Procedure

$\text{Bi}_{0.8}\text{Er}_{0.2}\text{O}_{1.5}$ (ESB) was synthesized by conventional solid-state synthesis using Bi_2O_3 (99.8%, Aldrich) and Er_2O_3 (99.99%, Aldrich) powders. The powders were Ball-milled for 24 h using zirconia balls, and then the powders were sieved using a 300 mesh sieve. Subsequently, the resulting powders were calcinated at 800°C for 10 h. The $(\text{Bi}_{0.8}\text{Er}_{0.2}\text{O}_{1.5})_{0.95}(\text{ZrO}_2)_{0.05}$ (ZESB) powder doped with 5 mol % Zr was synthesized by the same method using Zr_2O_3 (99.99%, Aldrich) powder as a dopant. $(\text{Bi}_{0.8}\text{Er}_{0.2}\text{O}_{1.5})_{0.98}(\text{CaO})_{0.02}$ (CESB) powder doped with 2 mol % Ca was synthesized by the same method using CaCO_3 (99.99%, Aldrich) as a dopant. X-ray diffraction (XRD, RIGAKU D/MAX-2500) was used to verify if the powders were well synthesized, and X-ray diffraction pattern analysis in the 2θ range from 20° to 80° was obtained using $\text{CuK}_{\alpha 1}$ ($\lambda_{\text{CuK}\alpha} = 1.5406 \text{ \AA}$ at room temperature. Pellets

having a diameter of 10 mm were prepared by using a calcinated powder. The pellets were uniaxially pressed using Cold isostatic pressing (CIP) at 200 MPa. Then the pellet was sintered in air at 890°C for 16 h. $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (GDC) powder was purchased from Aldrich. Pellets having a diameter of 10 mm were prepared by using a GDC powder. The pellets were uniaxially pressed using CIP at 200 MPa, and the sample was sintered at 1500°C for 12 h. 8 mol% Y doped ZrO_2 (YSZ) polycrystalline substrate with a size of $1 \text{ cm} \times 1 \text{ cm} \times 0.5 \text{ cm}$ and a 8 mol% Y doped ZrO_2 (YSZ) single-crystal [100] substrate with a size of $1 \text{ cm} \times 1 \text{ cm} \times 0.5 \text{ cm}$ were used; both were purchased from MTI KOREA. To measure the impedance spectra, Pt paste was applied on both sides of the pellets, and then samples were sintered at 800°C for 2 h in air to make electrodes. The ionic conductivity of the samples was measured by using an EIS (VSP-300, Biologic) over a frequency range of 1 Hz to 5 MHz with a voltage amplitude of 50 mV. The measurement data were analyzed using the EC-Lab software program (ver. 11.02). For the analysis of the microstructure, all samples were thermally etched at 800°C for one minute and GDC were thermally etched at 1300°C for one minute, and the microstructures were observed using SEM (Hitachi SU5000).

3. Results and Discussion

3.1 Microstructural and structural characterization

A cubic crystal structure (space group of Fm-3m) δ - Bi_2O_3 has a stable phase from 723°C to 825°C , the melting point.²⁴ On cooling below 723°C , δ - Bi_2O_3 is transformed to monoclinic Bi_2O_3 . Doping the cubic δ - Bi_2O_3 with cations with high polarizability is known as an effective method of stabilizing the cubic δ - Bi_2O_3 phase. Among the high polarizability cations, Er has a relatively small ionic radius and can stabilize δ - Bi_2O_3 with a minimum amount of dopant. Doping δ - Bi_2O_3 with 20 mol% Er is the optimal doping concentration and showed the highest ionic conductivity.²⁵ In this work, ESB was doped with 2 mol % Ca. this is not at the same concen-

Fig. 2. Powder X-ray diffraction patterns of ESB, ZESB and CESB after 800°C calcination with index from ICDD card 00-034-0377, 03-065-3319.

tration of the zirconia dopant, 5 mol%. Because the solubility of Ca in ESB is lower than 5 mol%. XRD was performed to characterize the ESB, CESB, and ZESB powders calci-

nated at 800°C for 10 h. The XRD data showed that all the peaks of the ESB, CESB, and ZESB powders were well matched with the peak of δ - Bi_2O_3 , which had a cubic crystal structure (ICDD card 00-034-0377; $a=5.479$ Å) (Fig. 2). A small amount of γ - Bi_2O_3 , formed from slow cooling of δ - Bi_2O_3 , was detected in the ZESB and CESB powders; no other secondary phase was found. Size of the grains can be obtained from the cross-sectional SEM images; the images showed no secondary phase at the grain boundaries (Fig. 3). In addition, the SEM images also confirmed that the single-crystal YSZ has only one grain without a grain boundary, and confirmed that all the samples were sintered densely.

3.2. Brick layer model

Electrochemical Impedance spectroscopy is a very useful measurement method because the conductivity of the bulk and the grain boundaries can be separately measured in a polycrystalline material. In this study, the brick layer model was applied for impedance spectra analysis²⁷⁻²⁹. The description of the brick layer model is given a review article by Haile.²⁷ Fig. 4 shows the general circuit and a typical

Fig. 3. SEM image showing the cross section microstructures: (a) GDC with average grain size of 1.65 μm (b) polycrystalline YSZ with average grain size of 2.85 μm (c) single crystal YSZ, (d) ESB with average grain size of 6.51 μm (e) ZESB with average grain size of 4.1 μm (f) CESB with average grain size of 2.3 μm .

Fig. 4. A typical Nyquist plot and equivalent circuit of a polycrystalline material with brick layer model. Q is the constant phase element and R is the resistance.

Nyquist plot of polycrystals. The Nyquist plot is a plot in which the x-axis represents the real part of the impedance and the y-axis is the imaginary part of the impedance. The circuit consists of three RQ sub-circuits, wherein R ($Z_R = R$) denotes the resistance and Q the constant phase element (CPE). $Z_Q = [Y(j\omega^n)]^{-1}$, wherein $j = \sqrt{-1}$, ω is the frequency, Y and n are constants, and n is a value between 0 and 1. If n , which experimentally determines the characteristics of the RQ sub-circuits, is close to 1, the constant phase elements is similar to a capacitor, and Y is called the pseudo-capacitance. The frequency at the vertex of the semicircle shown in Fig. 4 is referred to as the characteristic frequency, ω_0 , of the sub-circuit RQ, which is expressed as $(YR)^{-1/n}$. If the frequency of that circuit is sufficiently different from another and n is close to 1, the resistance of each circuit can be calculated from the size of the arc on the real axis, and the capacitance of the sub-circuit is given as $(R\omega_0)^{-1}$. The resistance values are R_1 and R_2 of the RQ circuit. To associate these values with physical meanings, a cubic grain

Fig. 5. "Brick layer" model of a polycrystalline material. Grains are assumed to be cube-shaped, and grain boundaries exist as flat layers between grains.²⁹⁾

$$R_1 = \left(\frac{1}{R_{bulk}} + \frac{1}{R_{gb||}} \right)^{-1} \quad R_2 = R_{gb\perp}$$

$$Y = Y_{bulk} + Y_{gb||} \quad n = n_{bulk} + n_{gb||}$$

$$Q_1 = Q_{bulk} + Q_{gb||} \quad Q_2 = Q_{gb\perp} \quad Q_e$$

(b)

Fig. 6. Equivalent circuit models of a polycrystalline material with brick layer model. (a) Each component explicitly included in the circuit; (b) simplified equivalent circuit.

boundary model was assumed, wherein the model includes grain boundaries that are parallel or vertical to the applied field (Fig. 5).²⁷⁾ In Fig. 5, L denotes the length of the sample, A the cross-sectional area of the sample, d the edge length of a grain, and δ the thickness of the grain boundary. If $\delta \ll d$, the total length and the area of all samples for all the perpendicular (or series) grain boundaries is given by: $L_{\perp} = (\delta/d)L$ and $A_{\perp} = A$. Similarly, the total length and the area of all the parallel grain boundaries is given as $L_{||} = L$ and $A_{||} = (2\delta/d)A$. Fig. 6 shows the RQ sub-circuit corresponding to an ideal polycrystalline material. The first (RQ) circuit consists of parallel grain boundaries and grain interiors, and the second RQ circuit consists of the only series grain boundaries. The third CPE represents the electrode reaction. The equivalent circuit of Fig. 6(a) can be simplified, as done in Fig. 6(b) by combining the two parallel resistances into one simple resistance. Similarly, two CPEs can be merged into one Q . If the value of n is assumed to be the same, the entire pseudo-capacitance may be expressed as $Y_{gb||} = Y_{bulk}$ (Fig. 6(b)). In addition, as is known empirically, it was assumed that the low to mid frequency arc is related to the responses of grain boundaries in series with grain interior and the high frequency arc corresponds to the combined the response of grain interiors and parallel grain boundaries. Taking the specific conductivities of the grain boundary and the bulk are σ_{gb} and σ_{bulk} , respectively, and if the conduction in series and parallel grain boundaries follows the same mechanism, yield

$$\frac{1}{R_1} = \frac{1}{R_{gb||}} + \frac{1}{R_{bulk}} = \frac{A}{L} \left\{ \frac{2\delta}{d} \sigma_{gb} + \sigma_{bulk} \right\}, \quad (2)$$

$$\frac{1}{R_2} = \frac{1}{R_{gb\parallel}} = \frac{A}{L} \left\{ \frac{d}{\delta} \sigma_{gb} \right\}. \quad (3)$$

Defining $\sigma_i = L/A \left\{ \frac{1}{R_i} \right\}$, Eqs. (2) and (3) may be rewritten as follows:

$$\sigma_1 = \frac{2\delta}{d} \sigma_{gb} + \sigma_{bulk} \quad (4)$$

$$\sigma_2 = \frac{d}{\delta} \sigma_{gb} \quad (5)$$

From an impedance measurement and an information of the macroscopic sample dimensions, R_1 and R_2 can be obtained at once from the Nyquist plot, but σ_{gb} and σ_{bulk} cannot be obtained. However, the impact of the relative magnitudes σ_{gb} and σ_{bulk} on the relative magnitudes of R_1 and R_2 can be handled easily under various limiting conditions. The ratio of R_1 to R_2 can be obtained from the ratio between σ_1 and σ_2 .

$$\frac{\sigma_1}{\sigma_2} = \frac{R_2}{R_1} = 2 \left(\frac{\delta}{d} \right)^2 + \left(\frac{\delta}{d} \right) \frac{\sigma_{bulk}}{\sigma_{gb}} \quad (6)$$

As shown by the relation above, the ratio of R_1 and R_2 is related to both $(\sigma_{bulk}/\sigma_{gb})$ and (δ/d) .

Case (1): $\sigma_{bulk} > \sigma_{gb}$

For the situation where $\sigma_{bulk} > \sigma_{gb}$, the material generally has a microstructure with $\delta \ll d$. Therefore, Eq. (6) is reduced to:

$$\frac{\sigma_1}{\sigma_2} = \frac{R_2}{R_1} = \left(\frac{\delta}{d} \right) \frac{\sigma_{bulk}}{\sigma_{gb}}. \quad (7)$$

Similarly, Eq. (4) is reduced to:

$$\sigma_1 = \sigma_{bulk}. \quad (9)$$

Equation (8) is general assumption for impedance analysis to calculate bulk conductivity. The Nyquist plots of materials with $\sigma_{bulk} > \sigma_{gb}$ will present two distinguishable arc. if 1) R_1 and R_2 are comparable in magnitude, and 2) the characteristic frequencies of the two domains are sufficiently different. Materials with typical microstructure ($\delta/d < 1$ and $\sigma_{bulk} > \sigma_{gb} > 1$), will have $0.01 < R_1 < R_2 < 100$. Therefore, the first condition is met. The characteristic frequency of a material or a material domain is given by $w_0 = 1/RC$, wherein w_0 is a unique characteristic of a material that is independent to the geometric factors. Alternatively, w_0 can be expressed as $1/\rho\epsilon\epsilon_0$, wherein ρ is a resistivity given by $1/\sigma$, ϵ denotes the relative permittivity, and ϵ_0 denotes the vacuum permittivity. Therefore, the question whether $w_{0,bulk}$ is significantly different from $w_{0,gb}$ or not is eventually turned to whether $(\rho_{gb}\epsilon_{gb})$ is significantly different from $(\rho_{bulk}\epsilon_{bulk})$ or not. While resistivities of materials cover many orders of magnitude, dielectric constant do not significantly changed. Hence, $\epsilon_{bulk} \sim \epsilon_{gb}$ is a reasonable assumption. Therefore, the question is reduced to whether ρ_{bulk} is significantly different from ρ_{gb} or not. Since $\sigma_{bulk} > \sigma_{gb}$ is first

assumed, by definition $\rho_{gb} > \rho_{bulk}$, which eventually implies $w_{0,bulk} > w_{0,gb}$. Consequently, two arc will be presented in the Nyquist plot, and the semicircle at the low frequency will correspond to the responses of grain boundaries. More specifically, the characteristic frequency of the high frequency arc is determined as a combined the dielectric response of the grain interiors and parallel grain boundaries. However, since the parallel grain boundaries have an unfavorable geometric structure (a small area, and a long length), their contribution of the parallel grain boundary to the capacitance is negligible. In a typical microstructure, if $\sigma_{bulk} > \sigma_{gb}$, σ_{bulk} may be immediately obtained (Eq. 8). However, σ_{gb} requires the information about the grain size and the grain boundary (Eq. 5). In absence of microstructural observations, only d/δ can be directly estimated. Each RQ sub-circuit has a capacitance value. It can be obtained from the resistance and the characteristic frequency, and the two variables, Y and n of CPE which characterize the constant phase element. Specifically,

$$C = \frac{1}{Rw_0} = Y^{(1/n)} R^{\left(\frac{1}{n}-1\right)} \quad (9)$$

As mentioned above, due to the unfavorable geometry of the parallel grain boundary, the dielectric constant C_1 is related to the high frequency arc and it is entirely associated to the bulk. On the contrary, C_2 is related to the low frequency arc and it is almost exclusively associated to the vertical (or series) grain boundary. Therefore, C_1 and C_2 may be expressed as in the following equations:

$$C_1 \approx C_{bulk} = \frac{A}{L} \epsilon_{bulk} \epsilon_0, \quad (10)$$

$$C_2 \approx C_{gb\perp} = \frac{A}{L} \epsilon_{gb} \epsilon_0 \quad (11)$$

Since the overall dielectric characteristic of the bulk and the grain boundary is quite similar ($\epsilon_{bulk} \sim \epsilon_{gb}$),

$$\frac{C_2}{C_1} = \frac{\delta}{d} \quad (12)$$

Therefore, both the specific grain interior conductivity and the specific grain boundary conductivity can be measured by accurately using the relevant variables without microstructural observations.

Case (2): $\sigma_{gb} > \sigma_{bulk}$

In this case, for those materials which have typical microstructures, δ/d no greater than $1/100$, no simplification to Eq. (6) can be applied. Eq. (2) is applied to determine the shape of the Nyquist plot in the following three different sub-cases:

$$(a) \sigma_{gb} / \sigma_{bulk} \gg \frac{d}{2\delta} (R_{gb\parallel} \ll R_{bulk})$$

In this sub-case, $R_{gb\parallel}$ becomes dominant over R_1 ; the ionic transport along the parallel grain boundary is preferred to

the passage through the grain interiors

$$(b) \sigma_{gb} / \sigma_{bulk} \sim \frac{d}{2\delta} (R_{gb\parallel} \sim R_{bulk})$$

In this sub-case, since $R_{gb\parallel}$ is similar to R_{bulk} , the ionic transport occurs through both the parallel grain boundary and the grain interiors.

$$(c) \sigma_{gb} / \sigma_{bulk} \ll \frac{d}{2\delta} (R_{gb\parallel} \gg R_{bulk})$$

The resistance R_1 will be dominated by R_{bulk} . Therefore, the assumptions for Eqs. (7) and (8) are valid. As assumed above, if the dielectric constants of bulk is similar to that of grain boundaries and n is close to 1, the capacitance of the first RQ sub-circuit (Fig. 6(b)) may again be expressed as $C_1 \sim C_{bulk}$ in all the sub-cases. In the sub-cases (a) and (b), R_1 is within a factor of two $R_{gb\parallel}$. However, in sub-case (c), R_1 is close to R_{bulk} . In all the sub-cases, the second RQ circuit resistance, R_2 , is much smaller than R_1 . In sub-cases (a) and (b), R_2 may be expressed as in the following equation:

$$R_2 = R_{gb\perp} = 2R_{gb\parallel} \left(\frac{\delta}{d}\right)^2 \approx 2R_1 \left(\frac{\delta}{d}\right)^2 \quad (13)$$

On the other hand, in sub-case (c), R_2 may be expressed as in Eq. (7). In all the sub-cases, the capacitance of the second RQ circuit may be expressed as in the following equation:

$$C_2 = C_{gb\perp} = \frac{1}{2}C_{gb\parallel} \left(\frac{d}{\delta}\right)^2 \approx C_1 \left(\frac{d}{\delta}\right)^2 \quad (14)$$

The final approximation was based on Eq. (12). Since the responses of the first and the second sub-circuits are different, in the case of $\sigma_{gb} > \sigma_{bulk}$, the Nyquist plot theoretically exhibit two arcs. In contrast to what is generally observed results, the high frequency arc corresponds to the R_2Q_2 sub-circuit of the grain boundary in series with (or perpendicular to) grains, while low frequency arc corresponds to the combined R_1Q_1 sub-circuit of the parallel grain boundaries and grain interiors. This is the result of $R_2C_2 < R_1C_1$ (Eqs. (4), (10), and (11)). However, a two arcs spectrum is not actually be obtained, because the radius of the high frequency arc, R_2 , is several orders of smaller than low frequency arc. For example, if $\frac{\sigma_{gb}}{\sigma_{bulk}} \ll \frac{d}{2\delta}$ and $\delta/d = 1/100$, $R_2/R_1 = 10^{-4}$. Consequently, the Nyquist plot will exhibit a single arc.

Case (3): $\sigma_{gb} \sim \sigma_{bulk}$

For case (3), in which the grain boundary conductivity and the bulk conductivity of a material with typical microstructure are almost similar to those in case (1), $\sigma_{bulk} > \sigma_{gb}$. Eq. (6)

Fig. 7. Bulk ionic conductivity of all samples. Data are plotted in Arrhenius form.

is reduced to Eq. (7), and Eq. (4) may be expressed as Eq. (8). The case in which two arcs are obtained in the Nyquist plot is almost the same as case (1): if (i) R_1 is different from R_2 by a factor of 10 to 1000 times, and (ii) $w_{0,bulk}$ is significantly different from $w_{0,gb}$. According to Eq. (7), The Raito R_2/R_1 is 1/100 or smaller, for typical microstructures. The ratio is relatively small but not too small to be indistinguishable in the Nyquist plot. However, under the assumption of $\epsilon_{bulk} \sim \epsilon_{gb}$, the characteristic frequencies, $w_{0,bulk}$ and $w_{0,gb}$, are almost identical. As a result, only single arc will be observed. In addition, if σ_{gb} is almost the same as σ_{bulk} , the σ_1 obtained from the single arc will be within 2% of the σ_{bulk} . In summary, only for $\sigma_{bulk} > \sigma_{gb}$, two arcs can be observed.

3.3. Electrochemical Impedance Spectroscopy

The ionic conductivity in the temperature range from 600 to 250°C was obtained by impedance analysis using the brick layer model. Since the electric conductivity of a ceramic material is thermally activated, the following Arrhenius equation was used:

$$\sigma T = \sigma_0 e^{-E_a/kT} \quad (15)$$

where E_a denotes the activation energy needed for ionic conduction, σ_0 is the pre-exponential factor, and k is the Boltzmann constant. The activation energy was obtained from the Arrhenius plot (Fig. 7). As shown in Table 1, the grain boundary activation energy (1.16 eV) of the YSZ polycrystals is higher than bulk activation energy (1.06 eV). Similarly, for GDC polycrystals, the grain boundary activation energy (0.97 eV) is higher than bulk activation energy (0.68 eV). In Fig. 8, an impedance spectra was obtained at low-temperature because the grain boundary arc can be

Table 1. Activation Energy of Each Sample

	polycrystalline YSZ	single crystal YSZ	polycrystalline GDC	polycrystalline ESB	polycrystalline ZESB	polycrystalline CESB
Bulk E_a (eV)	1.06	1.16	0.68	1.33	1.31	1.24
G.b E_a (eV)	1.16	-	0.97	-	-	-

Fig. 8. (a-d) Nyquist impedance plots obtained from polycrystalline YSZ, single crystal YSZ, polycrystalline GDC, and single crystalline $Ce_{0.69}Gd_{0.31}O_{2-\delta}$ (GDC) impedance spectra data; (d) is from ref. 30.

obtained at a low temperature. Two arcs of the bulk and the grain boundaries in polycrystalline YSZ were obtained (Fig. 8(a)). Since two arcs, which represented in the polycrystalline, corresponds to Case 1 ($\sigma_{bulk} > \sigma_{gb}$) of the brick layer model. Only one arc corresponding to the bulk was obtained in the single crystal (Fig. 8(b)). Also, for polycrystalline GDC, two arc of the bulk and the grain boundary was obtained at 260°C in the Nyquist plot (Fig. 8(c)), which corresponds to Case 1 ($\sigma_{bulk} > \sigma_{gb}$). The impedance spectra data for single crystal GDC were obtained from the previous study because we cannot find GDC single crystal³⁰⁾ As expected, only single arc is obtained the single crystal GDC because of the absence of the grain boundary. As can be seen in Fig. 9(d), (e), and (f), although ESB is polycrystalline material, grain boundary arc cannot be obtained in the Nyquist plot. ESB did not have a grain boundary blocking effect caused by the space charge layer because ESB has no aliovalent dopant which causes segregation at the grain boundaries, in contrast to acceptor doped zirconia and acceptor doped ceria (Fig. 1). We believed that CESB (Eq. (1b)) will have a grain boundary effect, because the segregation of Ca'_{Bi} at the grain boundary will make space charge layer similar to the case of acceptor doped zirconia and ceria.¹²⁻¹⁵⁾ Likewise, we also believed that ZESB (Eq. (1a)) have a grain boundary effect because the segregation of Ca'_{Bi} at the grain boundary will cause a space charge layer.

However, only single arc, not two arcs is obtained in the Nyquist plot form both CESB and ZESB. This means that the blocking effect due to the space charge does not exist in $\delta-Bi_2O_3$. The resistance of the ESB at 275°C is 132.6 $k\Omega cm$, but that of CESB is lower, 75.6 $k\Omega cm$. The activation energy of CESB is 1.23 eV, which is also lower than that of ESB (1.33 eV). The resistance of ZESB at 275°C is 147 $k\Omega cm$, which is about 10% higher than that of ESB. The activation energy of ZESB is 1.31 eV, which was similar to that of ESB (1.33 eV). The lower resistance and the lower activation of CESB may be due to the increased oxygen vacancy concentration resulting from acceptor doping. The increased resistance in ZESB probably is due to the decreased oxygen vacancy concentration resulting from donor doping. This result is consistent with a previous study conducted with Y-stabilized $\delta-Bi_2O_3$ doped with Zr or Ca.³¹⁾ The absence of the space charge effect in the cubic bismuth oxides, regardless of the acceptor or donor doping, may have been because of the high oxygen vacancy concentration of $\delta-Bi_2O_3$ itself (25%).⁸⁾ The oxygen vacancy depletion in the space charge layer was proposed as the cause of the grain boundary blocking effect.²⁾ In $\delta-Bi_2O_3$, the oxygen vacancy depletion in the space charge layer may be negligible, because the oxygen vacancy concentration of $\delta-Bi_2O_3$ was much higher (25%) than that of 8YSZ (oxygen vacancy concentration: 8%) and GDC (oxygen vacancy concentration: 10%). In addition,

Fig. 9. (a-c) Impedance spectra from polycrystalline ESB, ZESB and CESB.

according to the brick layer model, the cases in which a single impedance arc is obtained are Case 2 ($\sigma_{bulk} \sim \sigma_{gb}$) and Case 3 ($\sigma_{bulk} < \sigma_{gb}$). Therefore, the grain boundary ionic conductivity of $\delta\text{-Bi}_2\text{O}_3$ should be similar to or higher than the bulk ionic conductivity, because of the high oxygen vacancy concentration and the high ionic conductivity at the grain boundary, $\delta\text{-Bi}_2\text{O}_3$ is almost free from the space charge effect, unlike other fluorite-type structure materials, thus it does not show the grain boundary blocking effect. An oxygen diffusion study of Bi_2O_3 conducted by oxygen tracer diffusion measurements demonstrated that Grain boundary ion diffusion in $\alpha\text{-Bi}_2\text{O}_3$ is three to four magnitude higher than bulk at 600°C , which is similar to the oxygen ion diffusion rate in bulk $\text{Ce}_{0.7}\text{Gd}_{0.3}\text{O}_{1.85}$.³²⁾ In short, the main mechanism of the ionic conduction in $\delta\text{-Bi}_2\text{O}_3$ may be through the grain boundaries. To prove this theory more directly, fur-

ther studies need to be conducted to observe the dopant segregation at the grain boundaries of ZESB and CESB through TEM and EELS and the space charge potential through KFM, which will demonstrate more direct experimental evidences that Space charge effect is negligible in cubic bismuth oxide.

4. Conclusions

In this work, an electrochemical impedance analysis was performed to investigate the grain boundary blocking effect due to the space charge in fluorite-type structured YSZ, GDC, ESB, ZESB, and CESB. The results showed that two distinguishable arcs were obtained in the Nyquist plot of polycrystalline YSZ and GDC, which confirmed the presence of the grain boundary blocking effect. The single-crystal materials with no grain boundary have only one arc, as expected. However, polycrystalline ESB and ZESB, and CESB have only one arc, indicating the absence of the grain boundary blocking effect caused by the space charge. The absence of the blocking effect in $\delta\text{-Bi}_2\text{O}_3$ may be because the intrinsic oxygen vacancy concentration in $\delta\text{-Bi}_2\text{O}_3$ is as high as 25% due to crystal structure. In addition, by applying the brick layer model for the impedance analysis, we demonstrate that grain boundary ionic conductivity of $\delta\text{-Bi}_2\text{O}_3$ is or even higher than bulk ionic conductivity ($\sigma_{bulk} \leq \sigma_{bg}$). Therefore, in this study we indirectly demonstrated that for $\delta\text{-Bi}_2\text{O}_3$, grain boundary may be a main ionic conductivity path unlike other fluorite-type materials and grain boundary blocking effect is absence using impedance analysis.

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