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Electrical properties of $(Bi_2O_3)_{0.75}(RE_2O_3)_{0.25}$ ceramics (RE = Dy, Y, Ho, Er and Yb)

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Abstract

Five kinds of rare earth stabilized bismuth oxide ceramics, $(Bi_2O_3)_{0.75}(RE_2O_3)_{0.25}$ (RE = Dy, Y, Ho, Er and Yb), were synthesized by sintering a mixture of Bi_2O_3 and RE_2O_3 at 900–1100 °C and their electrical properties were investigated. The bulk density and the lattice constant linearly increased with an increase in the atomic weight of RE and the ionic radius of RE^{3+}, respectively. The electrical conductivity at 300 °C slightly increased with the increasing ionic radius of RE^{3+}, while at 500 and 700 °C, it was constant regardless of the ionic radius of RE^{3+}. The migration activation energy and the association activation energy showed a maximum value and a minimum value at RE = Er, respectively.

Keywords: C. Electrical properties; C. Ionic conductivity

1. Introduction

Various kinds of ionic conducting ceramics such as $(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$, $(ZrO_2)_{0.85}(MgO)_{0.15}$, $(CeO_2)_{0.78}(GdO_{1.5})_{0.22}$ and $(Bi_2O_3)_{0.75}(Y_2O_3)_{0.25}$ having a fluorite-type structure, while the perovskite-type oxides, $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_3$ and $BaTh_{0.9}Gd_{0.1}O_3$, and $La_{10}Si_6O_{27}$ and $La_{9.33}(GeO_4)_6O_2$ having an apatite-type structure, are well known as oxide ionic conductors. Especially, the stabilized zirconia ceramics have been utilized as air/fuel ratio sensors in gasoline engines and as oxygen sensors for the measurement of the oxygen concentration in molten metal. Since $(Bi_2O_3)_{0.75}(Y_2O_3)_{0.25}$, $BaTh_{0.9}Gd_{0.1}O_3$ and $La_{10}Si_6O_{27}$ ceramics show the highest oxide ionic conductivities even below 500 °C, they are expected to be promising materials in many applications at lower operating temperatures. Among them, the stabilized bismuth oxide ceramics were developed as oxide ionic conductors by Takahashi and Iwahara [1–4]. After the reports of Takahashi and Iwahara, many research groups investigated these stabilized bismuth oxides, and recently, Azad et al. [5], Sammes et al. [6], and Verkerk and Burggraaf [7] have published the reviews. On the other hand, the $(Bi_2O_3)_{1-x}(RE_2O_3)_x$ ceramics stabilized with the trivalent rare earth ion (RE^{3+}) are convenient materials for examining the relationship between the ionic radius of RE^{3+} and the electrical properties. However, there are only a few reports on the $(Bi_2O_3)_{1-x}(RE_2O_3)_x$ ceramics stabilized with a series of rare-earths (RE), which has been studied by only one research group.

In this study, we synthesized the rare earth stabilized bismuth oxide, $(Bi_2O_3)_{0.75}(RE_2O_3)_{0.25}$ (RE = Dy, Y, Ho, Er and Yb), having a cubic single phase and examined the relationship between the ionic radius of RE^{3+} and the electrical properties.

2. Experimental

For the synthesizing of the $(Bi_2O_3)_{0.75}(RE_2O_3)_{0.25}$ (RE = Dy, Y, Ho, Er and Yb) ceramics, bismuth oxide (Bi_2O_3) and the rare-earth oxides (Dy_2O_3, Ho_2O_3, Y_2O_3, Er_2O_3 and Yb_2O_3) were used as the starting materials. First, these two oxides were ball-milled in a plastic pot with zirconia balls and water for 16 h. The mixture was then dried in an oven at 100 °C and ground into a powder with a mortar and pestle. These powders were

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next put into an alumina crucible and calcined in air at 700 °C for 2 h. The calcined powder was ball-milled again for 16 h into a fine powder. After drying, these powders were pressed into small discs and sintered in air at 900°∼1100 °C. The sintered discs were 12 mm in diameter and 2 mm in thickness.

The crystal parameters were determined by powder X-ray diffraction (Rigaku MiniFlex) in the 2θrange of 20–60°using CuK_α with Si as the internal standard. After coating both sides of the disc with Pt paste, it was baked at 900 °C. The electrical properties of the prepared samples were measured using LCZ meters (YHP 4276A and 4277A) in the frequency range of 100 Hz–1 MHz. The sample was heated to 300 °C to eliminate the adsorbed water before the measurement.

3. Results and discussion

The relationship between the sintering temperature and the bulk density of $(Bi_2O_3)_{0.75}(Y_2O_3)_{0.25}$ (RE = Dy, Y, Ho, Er and Yb) is shown in Fig. 1. The highest densifications were obtained at 1000 °C for all the samples and the bulk density linearly increased with an increase in the atomic weight of RE. The phenomenon in which the bulk density decreases with the higher sintering temperature and the longer sintering time is observed also to the Al_2O_3 ceramics [8]. When the sintering progresses and it is assumed that three pores which exist in the grain boundary change to one pore, it is calculated that the pore volume increases $\sqrt{3}$ times.

The XRD results showed that all the samples consisted of a cubic single phase (JCPDS No. 33-223). The relationship between the ionic radius of RE^{3+} and the lattice constant at each sintering temperature is nearly linear as shown in Fig. 2 and the lattice constant monotonously increased with the increasing ionic radius of RE^{3+}. On the other hand, it was observed that the lattice constant decreases with an increase in the sintering temperature.

In order to determine the conductivity, a complex plane impedance analysis is performed. A typical complex impedance plot in a lower temperature region gives two semicircles. The one in the higher frequency region probably corresponds to the bulk component, whereas another in the lower frequency region corresponds to the grain boundary component. When the temperature increases, the size of the semicircle in the low frequency decreases compared with that in the high frequency and a spike, probably arising from the electrolyte-electrode behavior, is observed in the lower frequency. From these results, the conductivity (the sum of the bulk and grain boundary) is determined by extrapolation to zero reactance of the complex impedance plot in the lower temperature region. The conductivity data are parameterized by the Arrhenius equation;

$$\sigma T = \sigma_0 \exp(-E/kT)$$

where σ, σ_0, E, k and T are the conductivity, pre-exponential factor, activation energy, Boltzmann constant and absolute temperature, respectively. The typical Arrhenius plot and the relationship between the ionic

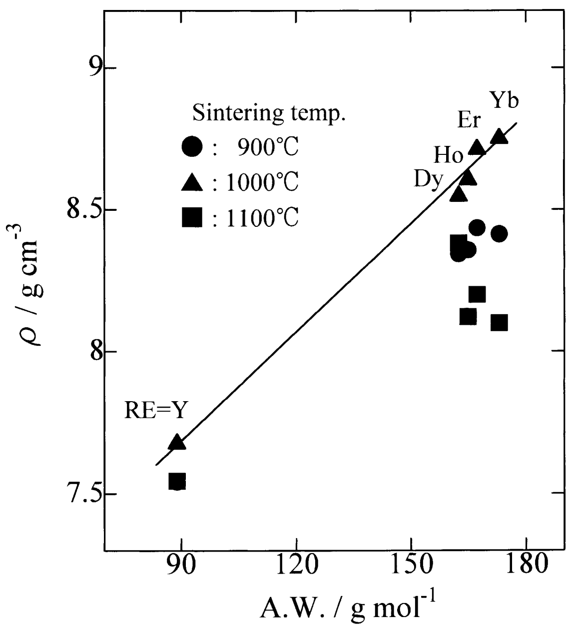

Fig. 1. Relationship between the atomic weight and the bulk density of $(Bi_2O_3)_{0.75}(RE_2O_3)_{0.25}$.

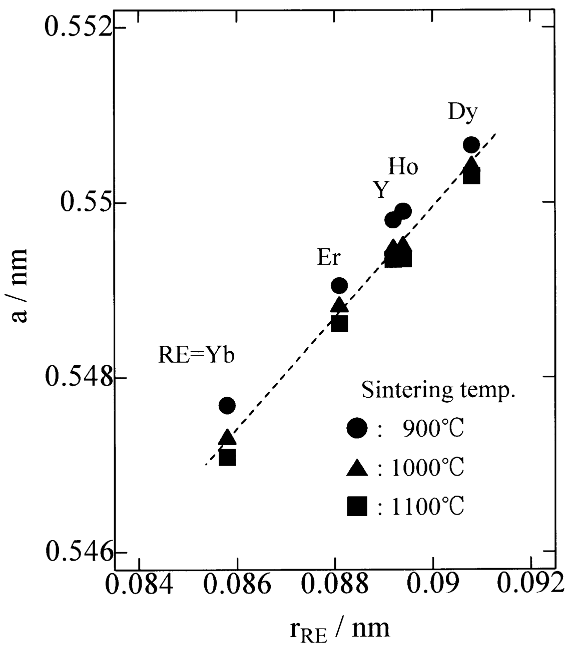

Fig. 2. Relationship between the ionic radius of RE^{3+} and the lattice constant of $(Bi_2O_3)_{0.75}(RE_2O_3)_{0.25}$.

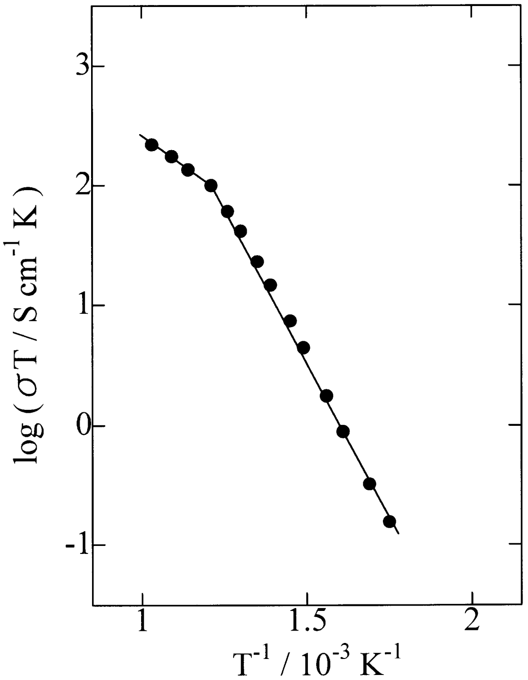

Fig. 3. Arrhenius plots of $(Bi_2O_3)_{0.75}(Er_2O_3)_{0.25}$ sintered at 1000 °C.

radius of RE^{3+} and the conductivities for the $(Bi_2O_3)_{0.75}(Y_2O_3)_{0.25}$ (RE = Dy, Y, Ho, Er and Yb) sintered at 1000 °C are shown in Figs. 3 and 4, respectively. Although the conductivity at 300 °C increased slightly with an increase in the ionic radius of RE^{3+}, those at 500 and 700 °C were almost constant. As seen in Fig. 3, inflection points appeared in the slopes of the Arrhenius plots around 550 °C. These results suggested that the conduction mechanism is different in the high temperature and low temperature regions. In general, the activation energy for conduction calculated from the slope of the Arrhenius plot can be assumed as the sum of the migration activation energy and association activation energy. Although the activation energy in the high temperature region is influenced only by the migration activation energy, that in the low temperature region is influenced by both the migration and association activation energy. Therefore, the association activation energy is estimated from the difference in the activation energy calculated from the slope in the low temperature and that in the high temperature region. The relationships between the ionic radius of RE^{3+} and the migration activation energy, and the association activation energy are shown in Fig. 5. The maximum value of the migration activation energy and the minimum value of the association activation energy were obtained at RE = Er. On the other hand, It was confirmed that the migration activation energy increased and the association activation energy decreased with an increase in the ionic radius of RE^{3+} for $(ZrO_2)_{0.91}(RE_2O_3)_{0.09}$ (RE = Gd, Dy, Y, Er and Sc) as reported by Arachi et al. [9] and $(ZrO_2)_{0.92}(RE_2O_3)_{0.08}$ (RE = Gd, Dy, Ho, Y, Er and Yb) by the authors [10].

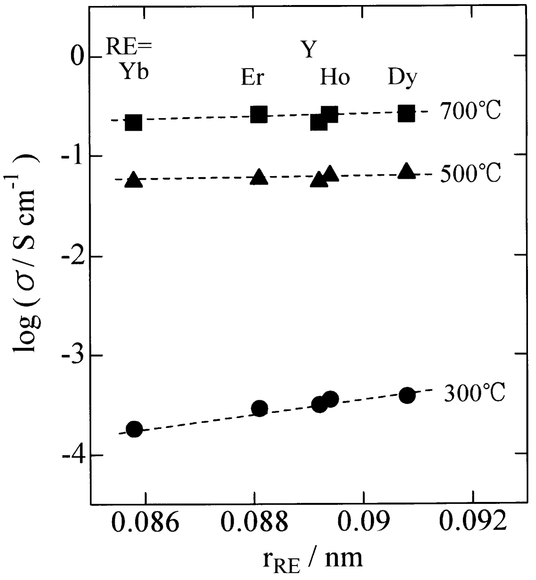

Fig. 4. Relationship between the ionic radius of RE^{3+} and the conductivity of $(Bi_2O_3)_{0.75}(RE_2O_3)_{0.25}$ sintered at 1000 °C.

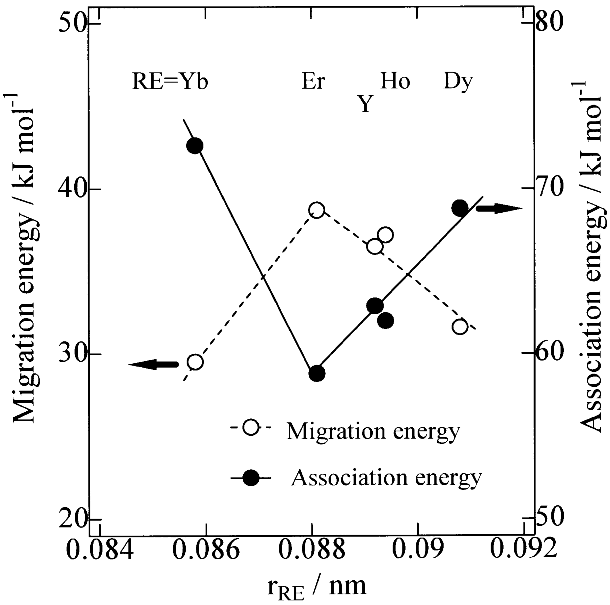

Fig. 5. Effect of the ionic radius of RE^{3+} on the migration energy and the association energy for $(Bi_2O_3)_{0.75}(RE_2O_3)_{0.25}$ sintered at 1000 °C.

4. Conclusions

The sinterability, the crystal structure and the electrical property of the $(Bi_2O_3)_{0.75}(RE_2O_3)_{0.25}$ (RE = Dy, Y, Ho, Er and Yb) ceramics were investigated. The highest densification was achieved by the sample sintered at 1000 °C and the bulk density linearly increased with an increase in the atomic weight of RE. The crystal system of the samples was cubic and the lattice constant monotonously increased with the increasing ionic radius of RE^{3+}. The conductivities at 500 and 700 °C were almost constant while those at 300 °C slightly increased with an increase in the ionic radius of RE^{3+}. The maximum value of the migration activation energy and the minimum value of the association activation energy were obtained at RE = Er.

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