

Conductivity of BaPrO₃ based perovskite oxides

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Abstract

To develop higher protonic conductivity, we have been studying a new perovskite-type oxide and found that BaPrO₃ based perovskite oxides showed high conductivity in a moist H₂ atmosphere. Their conductivity was about 0.1 S/cm at a temperature of 500°C and remained almost constant up to 700°C, which is much higher than that of Ba(Ce_{0.8}Gd_{0.2})O_{3-α}, Ba(Pr_{1-x}Gd_x)O_{3-α} prepared by solid state reaction exhibited an orthorhombic and/or cubic perovskite structure and with a high Gd content was stable in a reducing atmosphere. When Ba(Pr_{0.7}Gd_{0.3})O_{3-α} was used as an electrolyte, the open circuit voltage of the cell was about 1 V and this cell was able to operate at 500°C. During the testing of the cell, the formation of water on an air electrode led us to conclude that mobility of protons in the electrolyte occurred. The dominant conduction species in Ba(Pr_{1-x}Gd_x)O_{3-α} electrolyte were considered as oxygen ions and/or protons. © 1998 Elsevier Science S.A.

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1. Introduction

Solid oxide fuel cells (SOFCs) are expected to be high efficiency power generators. Because of the high operating temperature (1000°C), SOFCs lack in reliability of the construction materials in the stack and system. Perovskite-type oxides such as BaCeO₃, SrCeO₃, SrZrO₃ and CaZrO₃ have been known as high protonic conductors [1–6]. Among them BaCeO₃ has the highest conductivity. Recently, we investigated the adaptation of BaCeO₃ as an electrolyte for lower operation temperature (800°C) [7,8]. To operate at lower temperatures (400–600°C), development of higher protonic conduction is necessary for practical use. Therefore, we have been studying a new perovskite-type oxide which has a high protonic conductivity under 800°C.

The conductivity of these perovskite-type oxides (denoted ABO₃) depend on occupied sites in the crystal lattice of the fired material. The order of conductivity of these oxides was shown to be as follows: BaCeO₃ > SrCeO₃ > SrZrO₃ > CaZrO₃ [1–6]. In other words, this

order was Ba > Sr > Ca in the A site and Ce > Zr in the B site of the ABO₃ structure. To get higher conductivity of ABO₃ materials, it is predicted that lower electronegativity in the A site and easy reduction in the B site are necessary. We continued to develop new perovskite-type oxides in accordance with these rules and therefore, Pr was adopted as a B site element in ABO₃. Pr was adopted because of its non-stoichiometric property and easier reduction compared with Ce and Zr. In this study, we prepared BaPrO₃ based perovskite-type oxides and determined the crystal structure of them. The conductivity of such prepared oxides was also measured.

2. Experimental

Starting powders were prepared via the solid state reaction of BaCO₃, Pr₆O₁₁ and Gd₂O₃ at 1450°C for 10 h in air. The composition of the powders was Ba(Pr_{1-x}Gd_x)O_{3-α} at x = 0.1, 0.2, 0.3 and 0.4, and were named BPG91, 82, 73 and 64, respectively. Gd₂O₃ was added to improve the stability of the BaPrO₃ structure based on perovskite-type oxides in reducing atmospheres. The starting powders were

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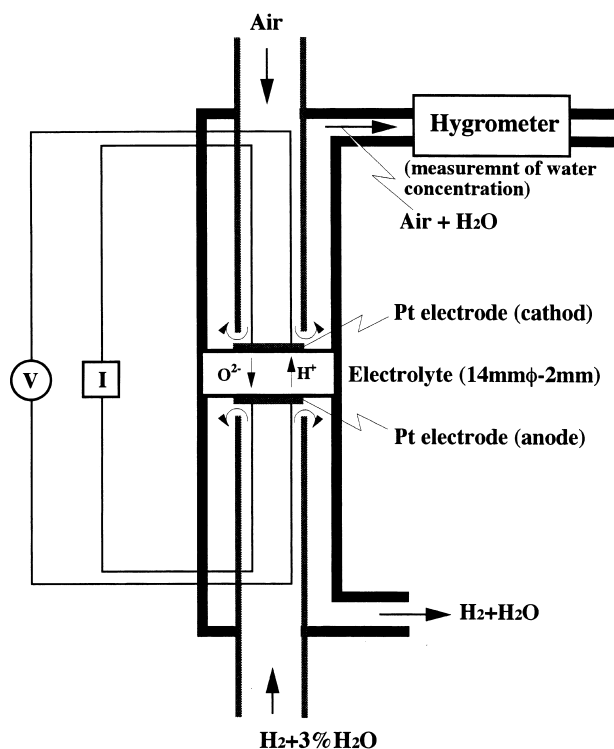


Fig. 1. Schematic illustration of SOFC test.

uniaxially pressed at 30 MPa and then isostatically pressed at 300 MPa into the compacts. The compacts were sintered at 1650°C for 2 h to obtain $\text{Ba}(\text{Pr}_{1-x}\text{Gd}_x)\text{O}_{3-\alpha}$ ceramics (named BPG). $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\alpha}$ ceramic (named BCG) was also prepared by the same method. The sintered samples were cut into regular bars ($3 \times 3 \times 30$ mm) and disks (14 mm diameter -2 mm thickness). The regular bars were

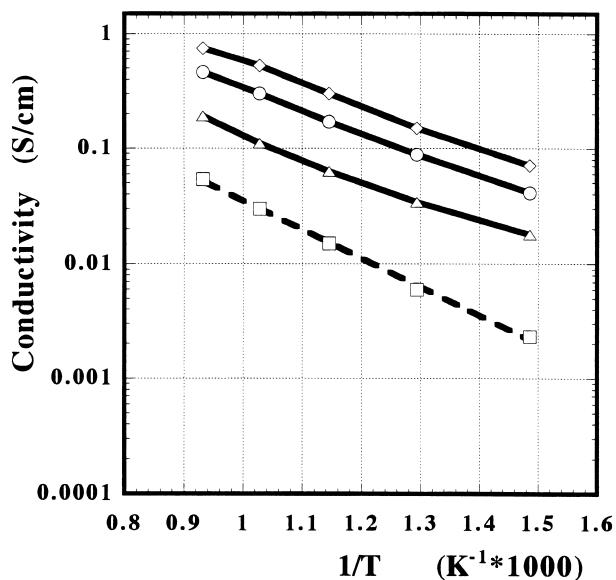


Fig. 2. Arrhenius plots of the conductivity of BPG and BCG in air: (\diamond) BPG82, (\circ) BPG73, (Δ) BPG64 and (\square) BCG82.

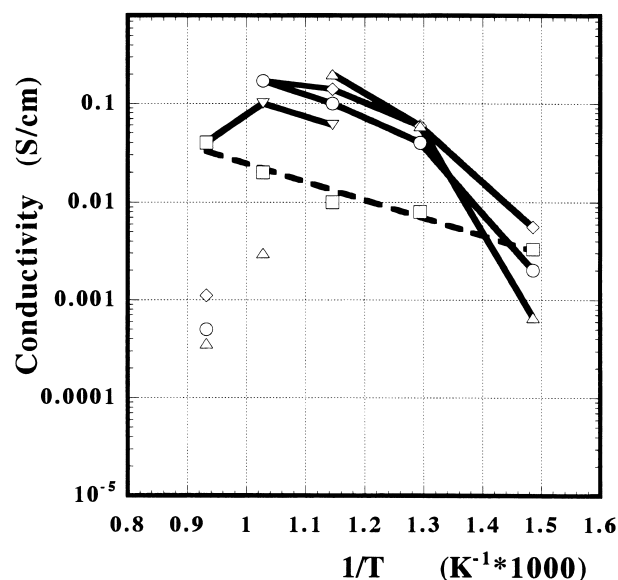


Fig. 3. Arrhenius plots of the conductivity of BPG and BCG in $\text{H}_2 + 3\% \text{H}_2\text{O}$: (∇) BPG91, (\diamond) BPG82, (\circ) BPG73, (Δ) BPG64 and (\square) BCG82.

connected by lead-in platinum wires to d.c. four-probes with platinum paste and were fired at 1000°C for 2 h. The electrical conductivity of BPG was measured by the d.c. four-probe technique in air and a moist hydrogen atmosphere. To evaluate SOFC performance and the ionic conductivity of BPG, platinum paste was screen printed on both sides of the disks and sintered at 1000°C for 2 h. The cell prepared in this way was set into the apparatus as illustrated schematically in Fig. 1. Fuel ($\text{H}_2 + 3\% \text{H}_2\text{O}$) and air were fed into a cell through an upper and lower tube at 500°C. The I - V characteristics and open circuit voltage were evaluated using an electrochemical measurement system (Hokuto Denko current pulse generator HC-111; Hewlett Packard digitizing oscilloscope 54201 and multimeter 3457A). The crystal structure of the starting powders and BPG samples was analyzed by X-ray diffraction (XRD) analysis using $\text{CuK}\alpha$ radiation (Phillips, PW1700).

3. Results and discussion

3.1. Electrical conductivity

Figs. 2 and 3 show Arrhenius plots of the total conductivity of BPG and BCG in air and moist H_2 atmospheres at 400–800°C, respectively. There is a linear relation between the logarithm of conductivity of BPG in air and the reciprocal temperature. This tendency is similar to a previously obtained result [9] and the measured conduction is due to electron holes (p-type). Moreover, it was confirmed by results of steam concentration cell measurements [9] that BPG in air shows no protonic conduction. The tendency of the conductivity of BPG in a moist H_2 atmosphere is

rather different from the result obtained in air. The relation between the logarithm of the conductivity and the reciprocal temperature is not linear and the conductivity decreases rapidly above 700°C. However, the conductivity in a moist H₂ atmosphere remained about 0.1 S/cm at 500–700°C.

3.2. Crystal structure

Fig. 4 shows XRD patterns of BPG82, 73 and 64, respectively. It can be seen that these samples consist of both orthorhombic and cubic phases; the intensity of the peaks of the cubic phase increases with increasing Gd content. XRD analysis of BPG powders calculated at 1450°C shows that only an orthorhombic perovskite structure was formed. Therefore, it was considered that the stable crystal structure of BPG at 1650°C was a mixture of orthorhombic and cubic phases.

Figs. 5 and 6 show XRD patterns of BPG82 and 73 exposed in a moist H₂ atmosphere, respectively. BPG82 in Fig. 5a consists of both orthorhombic and cubic phases. However, the peak of the orthorhombic phase in BPG82 shifts to a higher angle in comparison with the sintered

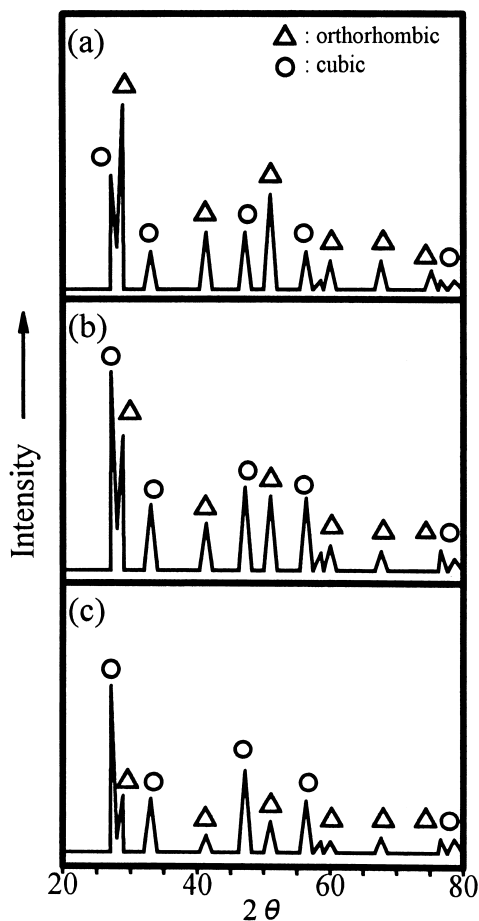


Fig. 4. X-ray diffraction patterns of BPG sintered at 1650°C: (a) BPG82, (b) BPG73 and (c) BPG64.

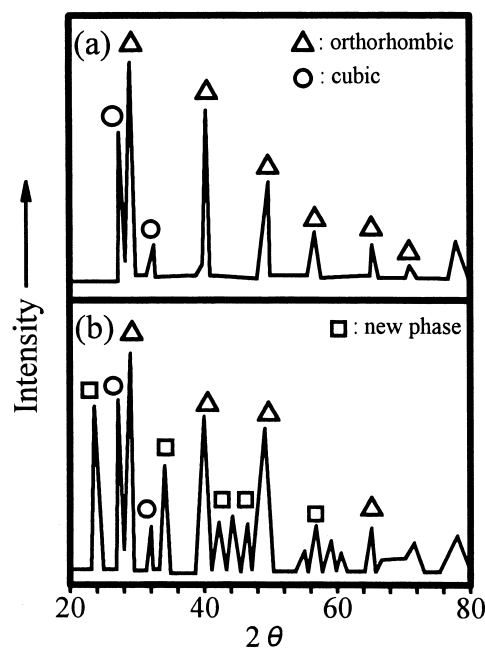


Fig. 5. X-ray diffraction patterns of BPG82 exposed in a moist H₂ atmosphere (a) at 600°C and (b) at 700°C.

sample. In other words, the lattice of BPG82 expanded due to the reduction of axis (the biggest expansion was measured for the C axis: 8.717 → 9.160 Å). Also, it is apparent from Fig. 5b that an unidentified phase forms in BPG82 when exposed to a moist H₂ atmosphere above 700°C. On the other hand, BPG73 exposed to a moist H₂ atmosphere below 600°C exhibits only a cubic structure (Fig. 6a). BPG consisting of mixed phases sintered at

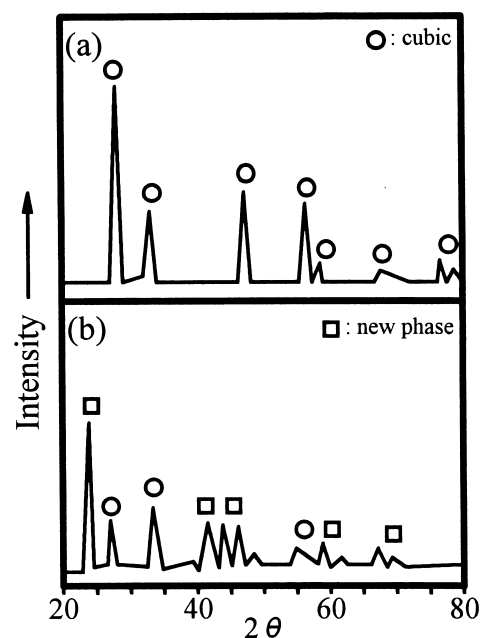


Fig. 6. X-ray diffraction patterns of BPG73 exposed in a moist H₂ atmosphere (a) at 400°C and (b) at 700°C.

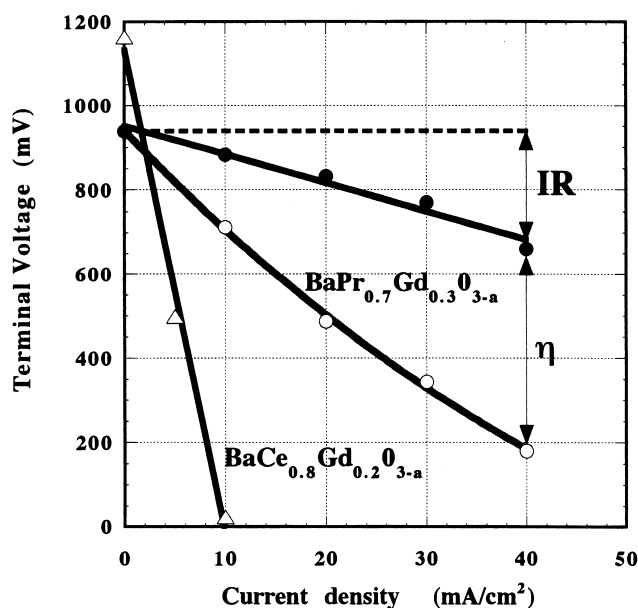


Fig. 7. I - V characteristic curves of a fuel cell with BPG and BCG as electrolyte at 500°C.

1650°C changes into a one phase structure, cubic phase, by exposure to a reducing atmosphere. Similar to BPG82, an unidentified phase also forms in BPG73 above 700°C (Fig. 6b).

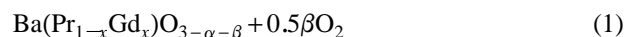
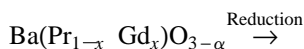
When the Gd content in BPG was less than $x = 0.2$ at $\text{Ba}(\text{Pr}_{1-x}\text{Gd}_x)\text{O}_{3-\alpha}$ (Gd-poor BPG), the structure of BPG in a reducing atmosphere becomes unstable because of the lattice expansion of the orthorhombic phase. On the other hand, BPG becomes stable in a reducing atmosphere when the Gd content was greater than $x = 0.3$ (Gd-rich BPG). The reason for this is that the main phase of Gd-rich BPG was cubic and the lattice of the cubic phase was stable in a reducing atmosphere. In both Gd-rich and -poor BPG, unidentified phases were formed and it was thought that formation of these phases caused the rapid decrease in conductivity of BPG.

3.3. Cell performance

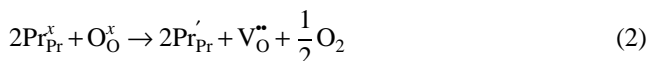
The overpotential (η) of Pt electrodes was measured by the current interruption method. Fig. 7 shows I - V characteristic curves when BPG73 electrolyte and BCG82 electrolyte were used at a temperature of 500°C. It is obvious from Fig. 7 that a cell with a BPG73 electrolyte can operate at 500°C, although lower current density can be derived during cell operation because of a high reaction resistance (η). The conductivity of BPG73 at 500°C calculated from Fig. 7 was about 0.04 S/cm and this value was similar to the result obtained from d.c. four-probe measurements (Fig. 3). The open circuit voltage of a cell with BPG is about 1.0 V, which is lower than that of a BCG cell. Therefore, we can conclude that the BPG cell contains electron or hole conductance. The protonic transport number of BPG was pre-

sumed to be about 0.2 using measurements of the water concentration on an air electrode. Therefore, BPG was regarded as a mixed conductor of protons, oxygen ions and holes.

In general, perovskite-type oxides such as BaCeO_3 and SrCeO_3 change into good ionic conductors due to M^{3+} doping ($\text{M} = \text{Gd}, \text{Y}, \text{Nd}$ etc.) [1]. However, BPG changes into an ionic conductor due to reduction. The peculiarity of conductivity of BPG causes Pr in the structure to behave as follows:



In other words



where $\text{V}_{\text{O}}^{\bullet\bullet}$ denotes oxygen vacancy. Pr_6O_{11} is a non-stoichiometric compound and Pr exhibits two valences (+3 or +4). It is thought that Pr in BPG also exhibits two valences and O in BPG comes out from lattice sites easily in a reducing atmosphere due to the valence deviation of Pr. Consequently, it was predicted that oxygen vacancy forms in the structure and ionic conductance is observed.

4. Conclusions

A new BaPrO_3 perovskite-type oxide exhibited unusual conductivity. It was considered that the conductivity resulted from a crystal structure change depending on the atmospheric conditions and behavior of Pr in the structure. The main results concerning the conductivity and crystal structure of the BaPrO_3 perovskite-type oxide are:

1. the electrical conductivity of $\text{Ba}(\text{Pr}_{1-x}\text{Gd}_x)\text{O}_{3-\alpha}$ was about 0.1 S/cm between 500 and 700°C.
2. $\text{Ba}(\text{Pr}_{1-x}\text{Gd}_x)\text{O}_{3-\alpha}$ exhibited an orthorhombic and/or cubic perovskite structure.
3. $\text{Ba}(\text{Pr}_{1-x}\text{Gd}_x)\text{O}_{3-\alpha}$ with rich Gd content showed cubic perovskite structure and was stable in reducing conditions at 400–600°C.
4. $\text{Ba}(\text{Pr}_{1-x}\text{Gd}_x)\text{O}_{3-\alpha}$ is regarded as a proton, oxygen ion and hole mixed-conductor.
5. we confirmed that SOFCs with the $\text{Ba}(\text{Pr}_{1-x}\text{Gd}_x)\text{O}_{3-\alpha}$ electrolyte can successfully operate at 500°C.

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