DEGRADATION OF RHOMBOHEDRAL (Y0.25Bi0.75)2O3 SOLID ELECTROLYTE

Chaur-Chi Huang, Kuan-Zong Fung
Department of Material Science and Engineering,
National Cheng Kung University
Tainan 70101, Taiwan, Republic of China

ABSTRACT

High temperature cubic $\delta$-Bi$_2$O$_3$ is well known to be the best ionic conductor due to its highly defective structure. As-sintered $\delta$-phase can be stabilized to lower temperatures by the addition of 25 mol% Y$_2$O$_3$. However, (Y$_{0.25}$Bi$_{0.75}$)$_2$O$_3$ undergoes phase transformation from cubic to rhombohedral phase after annealing at temperatures $\leq$650°C. The stability of Bi$_2$O$_3$-based solid electrolyte in water-containing environment is extremely important for SOFC applications. In this study, both cubic and rhombohedral (Y$_{0.25}$Bi$_{0.75}$)$_2$O$_3$ were immersed in water at 50°C. The microstructure, crystal structure and chemical analysis were examined by SEM, XRD, TEM, and EDAX. Cubic phase showed excellent stability in H$_2$O but rhombohedral phase was gradually attacked because of the unstable layered structure. From the XRD analysis conducted on reacted samples, the reaction products were found to be monoclinic $\alpha$-Bi$_2$O$_3$. At the extended period of water immersion, rectangular and needle-like crystals were observed by TEM. According to electron diffraction pattern observed, these two types of crystals were confirmed to be Y(OH)$_3$·xH$_2$O and Bi$_2$O$_2$CO$_3$ respectively. It is believed that the weakened Bi-O bonding plays an important role in the reaction of water and layered rhombohedral structure.

INTRODUCTION

Pure bismuth sesquioxide exhibits $\delta$-phase at high temperatures with fluorite structure. This material has the best oxygen ion conductivity of 1 S/cm at 800°C due to the 25 mol% oxygen vacancies. The $\delta$-Bi$_2$O$_3$ is only stable in the temperature range from 723°C to 823°C. Phase transformation of cubic to monoclinic $\alpha$-phase occurs at temperatures below
723°C. The formation of monoclinic α-phase and other metastable phase has been investigated in the past(1). For Bi₂O₃ to be a useful solid electrolyte, stabilization of δ-phase to lower temperatures is necessary. Doping 25 mol% yttrium into bismuth oxide does not only stabilize the fluorite structure but also maintains the high conductivity(2). Nevertheless cubic Y₀.₅Bi₁.₅O₃ slowly transforms into rhombohedral phase during the annealing process at 600°C(3).

With an oxygen conductor as solid electrolyte for SOFC, the water vapor will form at the electrolyte/anode interface. It is important to investigate the possible reaction between Bi₂O₃-based solid electrolyte and water. In alkine-earth oxide doped Bi₂O₃, the rhombohedral phase was found to be unstable and underwent unknown reaction in the humid environment as described by Watanabe(4). However the reaction between water and (Y₀.₂₅Bi₀.₇₅)₂O₃ has not been thoroughly studied. Therefore, the objective of this work was to study (1) the reaction mechanism for water and rhombohedral/cubic (Y₀.₂₅Bi₀.₇₅)₂O₃ , and (2) the effect of crystal structure on the kinetics of this reaction.

**EXPERIMENTAL PROCEDURE**

**Preparation of Y₀.₂₅Bi₀.₇₅O₁.₅**

Y₂O₃ (99.99% pure) and Bi₂O₃ (99.9% pure) were mixed in desired ratio followed by ball-milling in ethanol for 24h. After drying, the powder mixture was calcined at 900°C for 20h. After calcination, the agglomerates were ground and ball-milled again to obtain homogeneous and fine (Y₀.₂₅Bi₀.₇₅)₂O₃ powder. Disk-shaped pellets were formed by cold isostatic pressing at 20MPa. Subsequently, the green pellets were sintered at 950°C for up to 24h and then furnace-cooled to room temperature.

**Isothermal Annealing**

To obtain the rhombohedral phase in (Y₀.₂₅Bi₀.₇₅)₂O₃, the as-calcined powder and as-sintered samples were heated at 600°C for various periods of time from 200 to 400 hours.

**Conductivity Measurement**

The ionic conductivity of samples was measured using two-probe ac method. Platinum paste was applied on both faces of the sintered disks as electrodes and fired at 700°C for 1h. Silver wires were used as the lead wires connecting to both electrodes. Impedance was
measured over a range of frequencies between 20Hz and 1MHz using an HP-4284A LCR meter.

**Water Treatment**

The calcined powder, sintered, and annealed samples were immersed in water at 50°C for up to several hundred hours. After water treatment, water was carefully removed. XRD, TEM and DTA were conducted on the reacted sample for structure analysis and microstructure observation.

**Crystallographic Analysis**

X-ray diffraction (XRD) analysis was conducted on unreacted and reacted samples using Shimadzu X-ray Diffraction System (model XD-D1) with monochromated Cu Kα radiation. The accelerating voltage and current were set at 30kV and 30mA, respectively, with a 2θ scan speed of 2° min⁻¹ from 20° to 60°.

**Electron Microscopy**

Both SEM and TEM were used for the microstructure observation. The chemical composition of reacted samples was analyzed using EDAX.

**Thermal Analyses**

Differential thermal analyzer (Setaram TAG 24 Thermoanalyzer) was used for the thermal analysis. The analysis was conducted on reacted (Y₀.₂₅Bi₀.₇₅)₂O₃ powder with a heating rate of 5°C/min in the range from 25°C to 600°C in air.

**RESULTS**

**Cubic to Rhombohedral Phase Transformation**

δ-phase Y₀.₂₅Bi₀.₇₅O₁.₅ was calcined at 900°C for 20 hours and the XRD pattern is shown in Figure 1(a). Fluorite structure with 25mol% oxygen vacancies located at tetrahedral sites was obtained. This phase can be kinetically stabilized to low temperatures. When the as-sintered samples were annealed at 600°C, cubic phase became unstable and gradually transformed into rhombohedral phase. Figures 1(a), 1(b) and 1(c) revealed the XRD results.
of $\delta$-phase $Y_{0.25}Bi_{0.75}O_{1.5}$ annealing at 600°C for 200, 300 and 400 hours respectively. After annealing at 600°C for 400h, only small amount of cubic phase was observed. Most of the cubic phase has transformed into rhombohedral phase. From these X-ray patterns, the intensity of reflections representing rhombohedral phase was getting stronger and sharper as the annealing time increased.

It is known that alkaline earth metal oxides and $Bi_2O_3$ form stable rhombohedral solid solutions which exhibit good ionic conductivity. In the $Y_{0.25}Bi_{0.75}O_{1.5}$, the formation of rhombohedral phase causes not only the degradation of mechanical strength but also the loss of conductivity(5). Figure 2 shows the dynamic conductivity during the annealing process at 600°C. After 400 hours annealing at 600°C the conductivity decreased from $10^{-1.6}$ S/cm to $10^{-2.6}$ S/cm.

**XRD Analysis**

Since the cubic $\rightarrow$ rhombohedral transformation is inevitable, it is necessary to study the effect of water on the stability of cubic and rhombohedral phases in $Y_2O_3$-$Bi_2O_3$ solid electrolyte. The reaction of cubic/rhombohedral phase with aqueous solution was studied and four annealing conditions were examined (0hr, 200hr, 300hr, and 400hr). According to the XRD pattern shown in Figure 3, the reflection intensity of rhombohedral phase decreased drastically but not for the cubic phase. In additions, a third phase was observed in the reacted samples. The third phase was found to be $\alpha$-Bi$_2$O$_3$ with monoclinic structure.

In order to examine the reaction products in more detail, the reaction time was extended. After the powder was annealed at 600°C for 400 hours, the same sample was immersed in 25°C water for 180 days. The reacted powder was clearly segregated into two layers. The upper-layer was white and the lower-layer was yellow. These powders were separated and examined by means of X-ray diffraction analysis. The phase of the upper-layer powder was tetragonal Bi$_2$O$_2$CO$_3$ and the bottom-layer was a mixture of cubic, rhombohedral, and $\alpha$-Bi$_2$O$_3$. However, no yttrium-containing phase was observed in the XRD analysis.

**Scanning Electron Microscopy**

Figure 4(a) shows the micrograph of polished surface taken from the as-sintered sample which exhibits cubic structure. In Figure 4 (b), the micrograph was taken from the same sample after reacting with water at 50°C for 150 hours. Figure 4(b) shows that the polished surface degraded seriously. It suggests that either the reaction is accompanied by a volume change or significant decomposition has occurred.
TEM Analysis

In order to clarify the reaction observed, TEM and EDAX were used to analyze the microstructure and composition of reacted powder. Figure 5(a) and 5(b) show the TEM micrographs of the annealed powder aged in water for several months. The needle-like crystals were observed clearly from these two TEM micrographs, and the crystal size was about 30-50 nanometer. EDAX analysis of these fine crystals is presented in Figure 6. This needle-like structure from both upper and lower layer powders was composed of 34.52mol% yttrium and 34.52mol% oxygen. Because the diffraction pattern of the fine crystal rapidly changed with the exposed time under electron beam, the crystal structure couldn’t be determined precisely. From the DTA analysis, it is believed that the needle-shape crystal is an yttrium containing hydrated compound. According to diffraction patterns shown in Figures 7(a) and 7(b), the rectangular shaped crystal structure was a tetragonal Bi$_2$O$_2$CO$_3$ which is in excellent agreement with XRD results.

Differential Thermal Analysis

DTA results from upper and lower layers of powder aged in water for several months are presented in Figures 8(a) and 8(b). One endothermic peak and two exothermic peaks were found in both analyses. The first endothermic peak at 100°C was due to the vaporization of absorbed water molecule. The second and third exothermic peaks were found at 300°C and 500°C. According to Taichi's research(6), amorphous yttrium hydroxide containing crystal water dehydrates at 300°C and forms hexagonal Y(OH)$_3$. Furthermore, Y(OH)$_3$ decomposes into Y$_2$O$_3$ as the temperature increases up to 500°C. These results indicate that the presence of the exothermic peaks is caused by the decomposition of hydrated yttrium hydroxide.

DISCUSSION

Phase Transformation of (Y$_{0.25}$Bi$_{0.75}$)$_2$O$_3$ from δ-Phase to Rhombohedral Phase

Although the addition of 25% Y$_2$O$_3$ could effectively keep the δ-phase from transforming into a monoclinic α-phase, this result indicates that the δ-phase actually is a metastable phase. After annealing at temperatures lower than 650°C for several hundred hours, the orange color δ-phase could transform into a yellowish rhombohedral phase. This result also suggests that the highly defective δ-phase tends to transform into a more compact rhombohedral structure. Thus, a lower conductivity of rhombohedral phase (10$^{-2.6}$ S/cm at 600°C) than that of cubic phase (10$^{-1.6}$ S/cm at 600°C) is expected.
After the powder containing rhombohedral phase was immersed in water for a certain period of time, the rhombohedral phase decomposed into $\alpha$-Bi$_2$O$_3$ and a yttrium containing compound. With extended reaction, the $\alpha$-Bi$_2$O$_3$ is believed to react with CO$_2$ and form Bi$_2$O$_2$CO$_3$ as clearly shown in XRD traces (Figure 3). However, the cubic $(Y_{0.25}Bi_{0.75})_2O_3$ solid solution remains unchanged based on XRD analysis and micrograph observation although the cubic $(Y_{0.25}Bi_{0.75})_2O_3$ is a more defective structure.

The rhombohedral phase of $(Y_{0.25}Bi_{0.75})_2O_3$ is iso-structural with the rhombohedral phase in MO-Bi$_2$O$_3$ (M=Ca, Sr and Ba) system which is a layered structure(7,8). Each unit cell contains 3 (Y-Bi)-O blocks. Each block contains 3 cation layers and 2 oxygen layers. Each block is bonded by van der Waal’s force. Therefore, the samples with rhombohedral structure exhibit plate-like microstructure and have low mechanical strength. The inter block distance was estimated to be 2.975Å. Such a large open space provides an ideal channel for the transport of smaller size molecule of water.

After water molecules diffuse into the lattice, it is believed that the yttrium hydrated compound was formed. The presence of yttrium hydrated compound in the reacted $(Y_{0.25}Bi_{0.75})_2O_3$ powder was observed from TEM and DTA analysis. The extraction of yttrium ions from the rhombohedral blocks by water molecules also destabilizes the structure when the water reaction proceeds. Therefore, $\alpha$-Bi$_2$O$_3$ found in the reacted powder is also expected. When $\alpha$-Bi$_2$O$_3$ remained in water for long enough time, Bi$_2$O$_2$CO$_3$ was found as shown in Figure 3. The formation of Bi$_2$O$_2$CO$_3$ was caused by the reaction of dissolved CO$_2$ and $\alpha$-Bi$_2$O$_3$.

**Effect of Structure on the Water Reaction**

For the as-sintered $(Y_{0.25}Bi_{0.75})_2O_3$ samples that exhibit fluorite structure, no reaction was observed after the sample was exposed in water for 20 days. Since the cubic $\rightarrow$ rhombohedral transformation is a composition-invariant transformation, such a big difference in structural stability between these two phases must be caused by the difference in crystal structure. The phase transformation of cubic to rhombohedral phase can be viewed as sublattice rearrangement of oxygen layer located at tetrahedral site by removing oxygen from third layer, filling into the existing oxygen vacancies and forming blocks with 3 layers of cation and 2 layers of oxygen. Then the blocks slide 1.3124Å along the basal plane and form a rhombohedral structure as shown in Figure 9.

Therefore, one of major differences between cubic and rhombohedral structure is the
missing oxygen layer which may provide the perfect path for water to react with metal ions in the rhombohedral phase. For cubic \((Y_{0.25}Bi_{0.75})_2O_3\), the distance between cation and oxygen layer is 1.5824Å. Considering the space occupied by the cation and oxygen ions, it is difficult for water molecules to move in between layers in the cubic structure. Thus, the cubic phase is basically immune to the water reaction.

**CONCLUSIONS**

The following conclusions may be drawn based on the present work:

1. \(\delta-(Y_{0.25}Bi_{0.75})_2O_3\) is a metastable phase which gradually transforms into a low-conductivity rhombohedral phase when annealed at 600°C.

2. After the reaction between water and the rhombohedral phase, the yttrium hydroxide compound and \(\alpha-Bi_2O_3\) were observed. Such a reaction was accompanied by a significant volume change which deteriorated the structure. It is believed that \(\alpha-Bi_2O_3\) further reacts with dissolved CO2 and forms Bi2O2CO3 as seen from XRD and TEM analyses.

3. Fluorite-type cubic phase did not react with water because of the close-packed layer and strong ionic bonding. Rhombohedral phase, on the other hand, was very unstable and decomposed easily in water. The reason is that the interblock space in the rhombohedral phase provides excellent path for the transport of water molecules.

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Fig 1 XRD pattern of (a) as-sintered sample and samples annealed at 600°C for (b) 200hr, (c) 300hr, and (d) 400hr.

Fig 2 The dynamic conductivity curve for the sample annealed at 600°C for 400 hours.
Fig 7 Diffraction pattern of the rectangular crystal which was found to be $\text{Bi}_2\text{O}_3\text{CO}_3$.

Fig 8 DTA from water reacted powder in (a) upper layer and (b) lower layer powder.

Fig 6 EDAX of the needle-like crystal. Fig 9 Rhombohedral structure viewed along $c$ axis.
Fig 3 XRD of powder taken from reacted samples in (a) upper-layer and (b) lower-layer.

Fig 4 SEM micrographs of (a) as-sintered sample and (b) the sample annealed and reacted with water.

Fig 5 TEM micrographs taken from water-reacted powder in (a) upper-layer and (b) lower-layer powder.