Oxygen Absorption Behavior of Ce$_2$Zr$_2$O$_{7+x}$ and Formation of Ce$_2$Zr$_2$O$_{7.5}$

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Oxygen absorption behavior of Ce$_2$Zr$_2$O$_{7+x}$ (0 ≤ x ≤ 1) with an ordered arrangement of Ce and Zr ions was studied by X-ray powder diffraction, electron microscopy and thermogravimetric analysis. It was noted that the oxygen absorption of Ce$_2$Zr$_2$O$_7$ during heating in oxygen proceeds mainly through two reactions: (1) reaction from Ce$_2$Zr$_2$O$_7$ to Ce$_2$Zr$_2$O$_{7.5}$ around 400 K and (2) reaction from Ce$_2$Zr$_2$O$_7$ to Ce$_2$Zr$_2$O$_8$ around 600 K. This behavior suggests the presence of the intermediate phase, Ce$_2$Zr$_2$O$_{7.5}$. The intermediate phase was found to give extra reflections compared with Ce$_2$Zr$_2$O$_7$, and it belongs to space group Fd$ar{3}$m. This intermediate phase was obtained by oxidation of Ce$_2$Zr$_2$O$_7$ at room temperature for about 1 year, or heating at 473 K or lower temperature in oxygen.

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1. Introduction

Ceria-based materials play an important role as an oxygen supplier as well as an absorber in an automotive exhaust emission control systems because of their high oxygen storage and release capacity through redox processes of Ce$^{4+}$/Ce$^{3+}$ couple. In particular, CeO$_2$–ZrO$_2$ solid solution has much higher oxygen storage capacity than CeO$_2$ even at low temperature of 673 to 1073 K. Therefore, CeO$_2$–ZrO$_2$ solid solution is widely used as a promoter for the three-way catalyst. The catalytic activity of CeO$_2$ doped with ZrO$_2$ as the promoter has been studied by many researchers. The oxygen storage/release property, or the redox property of Ce$^{4+}$/Ce$^{3+}$, and the thermal stability of CeO$_2$ have been improved through the formation of CeO$_2$–ZrO$_2$ solid solution. The improvement of the oxygen storage/release property is of practical significance, but the mechanism for that is still unknown. The crystal structure of CeO$_2$–ZrO$_2$ solid solutions changes with the Ce/Zr ratio and by heat treatments. This diversity makes it difficult to understand the oxygen storage/release property of CeO$_2$–ZrO$_2$ solid solutions. A reduction treatment of the material at high temperature, especially above 1473 K, gives the CeO$_2$–ZrO$_2$ solid solution with better oxygen storage/release property, particularly the solid solution with around Ce/Zr = 50/50 (molar ratio). This treatment yields CeO$_2$–ZrO$_2$ solid solution with the ordered arrangement of Ce and Zr ions along (110) direction. Ce$_2$Zr$_2$O$_7$ with pyrochlore structure was formed by the reduction of CeO$_2$–ZrO$_2$ solid solution of the composition, Ce/Zr = 50/50. The objective of the present work is to investigate the correlation between existing phases and the oxygen storage property.
and selected area electron diffraction (SAED). XRD profile was measured with RIGAKU model RINT–2200 diffractometer using Cu Kα radiation. The lattice parameters of Ce₂Zr₂O₇₋ₓ were calculated from 7 intense and well-resolved diffraction peaks in the 2θ range from 25 to 75° using least-squares method. SAED patterns were obtained by a transmission electron microscope (TEM) (Model JEM–200CX, JEOL, Tokyo). Thermogravimetric (TG) analysis was made with RIGAKU model TG8110 thermobalance to calculate the amount of oxygen and to study the oxidation behavior. TG analysis was conducted up to 473 or 1073 K in flowing oxygen with heating rate of 5 K/min soon after each heat treatment.

3. Results and discussion

3.1 Oxygen absorption behavior at room temperature

XRD peaks of Ce₂Zr₂O₇ samples reduced at 1673 and 1773 K were identified by a single phase of Ce₂Zr₂O₇ with pyrochlore-type structure and cell parameter of 1.074 nm (Fig. 1(a)). The powder reoxidized at 1073 K, Ce₂Zr₂O₇, was a single Ce³⁺ phase with cell parameter of 1.053 nm (Fig. 1(b)). The lattice constant of Ce₂Zr₂O₇ decreased with oxidation time at room temperature in air, and it seems to saturate to the value of about 1.065 nm as shown in Fig. 2. The decrease is ascribed to the change from larger Ce³⁺ to smaller Ce⁴⁺ by the oxidation. The oxidation at room temperature finishes giving an intermediate phase with an intermediate lattice constant between those of Ce₂Zr₂O₇ and Ce₂Zr₂O₆. This saturation suggests the formation of an intermediate phase. The chemical composition of the intermediate phase was estimated to be Ce₂Zr₂O₇₋ₓ from the weight increase during oxidation at 1073 K under flowing oxygen (1.6%). The structure of Ce₂Zr₂O₇₋ₓ seems to be different from pyrochlore-type structure or Ce²⁺ phase as shown in Fig. 1(c).

3.2 Oxygen absorption behavior during heating

Figure 3 shows TG and DTG (differential thermal gravimetric) curves for Ce₂Zr₂O₇ prepared by the reduction at 1773 K. The measurement was started immediately after the reduction. The total weight change observed (2.9%) agrees well with the expected value of full oxidation (2.8%). This reaction consists mainly of two reactions: which show the shape DTG peak around 400 K and the broad DTG peak around 600 K. To determine the amount of absorbed oxygen of former reaction, TG analysis was conducted up to 473 K. The amount of absorbed oxygen of former reaction was 1.5% and the estimated composition was Ce₂Zr₂O₇₋₀.5. The weight increase was not observed during keeping at 473 K for 2 h. This result also suggests the formation of an intermediate phase.
Figure 4 shows TG and DTG curves for the powders Ce$_2$Zr$_2$O$_7$ oxidized at room temperature for 6 d and 1 year. TG curves above 473 K of these powders were similar, however those below 473 K were quite different. In particular, the amount of absorbed oxygen of the powder oxidized for 1 year is almost zero below 473 K. These results suggest that the reaction, which shows the sharp DTG peaks around 400 K, proceeds slowly in air at room temperature for 1 year, and proceeds rapidly around 400 K. Then after first reaction, Ce$_2$Zr$_2$O$_7$ changes to an intermediate phase Ce$_2$Zr$_3$O$_{12.5}$. Hereafter, the intermediate phase observed in this study is denoted as $\beta$-Ce$_2$Zr$_2$O$_{7.5}$.

3.3 Existing phase in Ce$_2$Zr$_2$O$_{7.5}$

The difference of XRD patterns of Ce$_2$Zr$_2$O$_7$ and $\beta$-Ce$_2$Zr$_2$O$_{7.5}$ are shown in Fig. 5. Extra reflection peaks marked with ▲ were observed for $\beta$-Ce$_2$Zr$_2$O$_{7.5}$. From $d$-value, these are considered to be 200, 600 and 640 reflection peaks, which should never be observed for pyrochlore-type structure with space group Fd$ar{3}$m. In order to confirm that these peaks of $\beta$-Ce$_2$Zr$_2$O$_{7.5}$ do not come from impurity phases, the electron diffraction pattern was examined (Figs. 6 and 7). The extra spots marked by arrow, which cannot be assigned to pyrochlore-type structure, are observed in SAED patterns, and they are assigned to 200 and 420 spots. The 200 spots are always observed during tilting from [110] to [100] zone axis (Fig. 8). Therefore, these spots would be caused by neither double diffraction nor impurity phases. The extra reflections observed for $\beta$-Ce$_2$Zr$_2$O$_{7.5}$ strongly suggest the formation of a new phase with a different symmetry from that of pyrochlore-type structure. The reflection conditions of $\beta$-Ce$_2$Zr$_2$O$_{7.5}$ determined from the results of XRD and SAED analysis are given as follows: $hk+l: h+k+l, h+l, l, h+l, h00: h$. If the conditions are even number, the corresponding diffractions will be observed. The space groups for the reflection conditions are F23, Fm$ar{3}$, F432, F$ar{4}$3m and Fm$ar{3}$m. In another respect, Fig. 2 suggests that the phase change from Ce$_2$Zr$_2$O$_7$ to $\beta$-Ce$_2$Zr$_2$O$_{7.5}$ is successive, that is, the two phase is closely similar. Therefore, possible cubic space groups for $\beta$-Ce$_2$Zr$_2$O$_{7.5}$ are Fd$ar{3}$, F4, F432 and F$ar{4}$3m which belong to the subgroups of Fd$ar{3}$m. From these considerations, $\beta$-Ce$_2$Zr$_2$O$_{7.5}$ phase is considered to belong to space group of F$ar{4}$3m. There is the other approach to determine the space group of $\beta$-Ce$_2$Zr$_2$O$_{7.5}$. Extra reflections of $\beta$-Ce$_2$Zr$_2$O$_{7.5}$ satisfy the rule, $h0l: h+l=2n$ as shown in Fig. 5. The extinction rule of $h0l: h+l=2n$ is made by diamond glide plane in Ce$_2$Zr$_2$O$_7$. This fact proves that the diamond glide plane in Ce$_2$Zr$_2$O$_7$ disappears during oxidation through from Ce$_2$Zr$_2$O$_7$ to $\beta$-Ce$_2$Zr$_2$O$_{7.5}$. The disappearance of diamond glide plane leads to the decrease in symmetry from space group F$ar{4}$3m to F$ar{4}$3m. Therefore, the space group of $\beta$-Ce$_2$Zr$_2$O$_{7.5}$ is again concluded to belong to the space group of F$ar{4}$3m.

In the literature, there are no reports on the new phase, $\beta$-Ce$_2$Zr$_2$O$_{7.5}$, observed in this study as far as we know. Baker et al. or Masui et al. reported new phases based on pyrochlore structure. However, they did not determine the space group and the concentration of oxygen experimen-
tally. Furthermore, their reoxidation temperature is too high to form β-Ce₂Zr₂O₇₋₅ phase. Therefore, the phases they observed are thought to be different from β-Ce₂Zr₂O₇₋₅ phase found in this study. Thomson et al. reported the phase Ce₂Zr₂O₇₋₃.₆ obtained by intercalation of oxygen into Ce₂Zr₂O₇ by chemical route. However, they have not found any evidence of the intermediate phase with the symmetry different from pyrochlore-type structure.

4. Conclusions
The relationship between oxygen absorption behavior and existing phases of Ce₂Zr₂O₇₋ₓ (0 ≤ x ≤ 1) with an ordered arrangement of Ce and Zr ions was studied by X-ray powder diffraction, electron diffraction and thermogravimetric analysis.

(1) The oxygen absorption of Ce₂Zr₂O₇ with pyrochlore structure proceeds through two-step reaction; reaction from Ce₂Zr₂O₇ to Ce₂Zr₂O₇₋ₓ around 400 K and reaction from Ce₂Zr₂O₇₋ₓ to Ce₂Zr₂O₇₋₅ around 600 K. This oxidation behavior indicates the presence of the intermediate phase of the composition, Ce₂Zr₂O₇₋₅.

(2) The intermediate phase, β-Ce₂Zr₂O₇₋₅, is determined to belong to space group F43m. β-Ce₂Zr₂O₇₋₅ can be formed by oxidation at room temperature for about 1 year, or heating at 473 K or lower temperature in oxygen.

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