Lattice parameter, defect concentration and oxygen diffusion in ceria solid solutions

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The results of x-ray diffraction, the size of lattice parameter, and the values of oxygen diffusion coefficient in YO1.5-CeO2, GdO1.5-CeO2, and NdO1.5-CeO2 systems were reviewed. In YO1.5-CeO2 system, the lattice parameter decreases as the concentration of YO1.5 increases. In GdO1.5-CeO2 system, the lattice parameter does not change very much. And in NdO1.5-CeO2 system, it increases as the concentration of NdO1.5 increases. When the oxygen diffusion coefficient was plotted as a function of lattice parameter, there was no correlation between them. However, when the oxygen diffusion coefficient was plotted as a function of the concentration of trivalent cation additives, there was very good correlation between them. Consequently, the diffusion coefficient does not depend on the size of crystal lattice in ceria solid solutions, but it depends on the concentration of trivalent cation additives.

Key words: CeO2, Y2O3, Gd2O3, Nd2O3, x-ray diffraction

1. INTRODUCTION

Cerium oxide is in fluorite structure. The oxides with fluorite structure have been known to exhibit very fast oxygen diffusion. The diffusion coefficient could be changed by doping the oxide with other metallic elements. Since the cerium oxide forms wide range of solid solution with rare earth elements, showing variety of lattice parameter, it is one of the ideal systems in which the relationship between the oxygen diffusion and the lattice parameter or the additives (solid solution) could be studied.

Among the solid solutions based on cerium oxide, YO1.5-CeO2, GdO1.5-CeO2, and NdO1.5-CeO2 are the systems in which oxygen diffusion coefficient has been determined. In this paper, some of the characteristics of CeO2-based solid solutions are reviewed. They are the results of x-ray diffraction, lattice parameters, and oxygen lattice diffusion coefficients. These data are used to explain the results of oxygen diffusion coefficients in terms of lattice parameter and defect concentration.

2. X-RAY DIFFRACTION

The x-ray diffractions for YO1.5-CeO2 system are shown in Figure 1. The x-ray diffraction pattern of undoped CeO2 corresponded to that of fluorite structure. At the low concentration of YO1.5, as the concentration of YO1.5 increased, the x-ray diffraction patterns were essentially the same. They were still in the fluorite structure. At the concentration of 40 % YO1.5, some of the satellite peaks were visible especially in the range of 2θ=35° to 45°. These satellite peaks combined with main fluorite peaks formed the x-ray diffraction pattern which was similar to that of rare earth C-type structure. However, the satellite peaks were very weak. At the higher concentration of YO1.5 (50-90 % YO1.5), these satellite peaks gradually grew while the main fluorite peaks still remained. At 100 % YO1.5, the structure is of course the rare earth C-type structure. The question is at which concentration of YO1.5 the crystal structure is the rare earth C-type. At this moment, there is no clear answer to the question. We need more studies in detail to clarify this.

The x-ray diffractions for GdO1.5-CeO2 system (not shown here) were almost the same as those for YO1.5-CeO2 system. In GdO1.5-CeO2 system the satellite peaks started to be seen at the concentration of 40 % GdO1.5. In the case of NdO1.5-CeO2 system, the x-ray diffractions are shown in Figure 2. At the low concentration of NdO1.5, the crystal was also in fluorite structure and at 45 % NdO1.5 and higher concentration, satellite peaks were seen. Since the structure of 100 % NdO1.5 is rare earth A-type structure, the x-ray diffraction pattern at 80 % NdO1.5-CeO2 was different: some peaks other than rare earth C-type and fluorite structures were seen. However, at the concentration between 5 and 75 % NdO1.5, the patterns were very similar to those of YO1.5-CeO2 and GdO1.5-CeO2 systems.
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Figure 1. X-ray diffraction patterns of Y₀₁.₅⁻Ce₀₂ system. Reprinted from ref. 4 with permission from Japan Society of Powder and Powder Metallurgy.

Figure 2. X-ray diffraction patterns of Nd₀₁.₅⁻Ce₀₂ system. a) x=80; b) x=75; c) x=70; d) x=65; e) x=60; f) x=55; g) x=50; h) x=45; i) x=40; j) x=35; k) x=30; l) x=25; m) x=20; n) x=15; o) x=10; p) x=5; and q) x=0, where x is mol % Nd₀₁.₅. ○, fluorite structure or rare earth C-type structure; △, rare earth C-type structure; ▲, rare earth A-type structure. Reprinted from ref. 6 with permission from American Ceramic Society.

Figure 3. Lattice parameters of Y₀₁.₅⁻Ce₀₂ and Gd₀₁.₅⁻Ce₀₂ systems. The data of Y₀₁.₅⁻Ce₀₂ were calculated from the data shown in Figure 1. Those of Gd₀₁.₅⁻Ce₀₂ are from the results of Ikuma et al.⁵

Figure 4. Lattice parameters of Nd₀₁.₅⁻Ce₀₂ system. Samples were fired at 1400°C. Data are taken from ref. 6 and re-plotted in this figure.
3. LATTICE PARAMETER

The lattice parameters of fluorite structure can be calculated using the x-ray diffraction results. They are shown in Figures 3 and 4.\(^{(1)}\)\(^{(6)}\) In order to calculate the lattice parameters in the range where there were no satellite peaks, all the peaks were used for the calculation. However, in the range where there were satellite peaks, only those peaks which corresponded to fluorite structure were used: satellite peaks were not used. This means that we assumed that the fluorite structure continues to exist even in the area where satellite peaks existed and where the crystal was in rare earth C-type structure. This kind of assumption is possible because fluorite structure and rare earth C-type structure are in a family of structures: if we take one quarter of the oxygen out of each unit cell in fluorite structure, and arrange the oxygen vacancy within the unit cell in a certain manner, we have rare earth C-type structure.

Figure 3 shows that in YO\(_1\),CeO\(_2\) system, the lattice parameter decreased gradually as the concentration of YO\(_{1.5}\) increased. The results agreed\(^{(5)}\) well with those\(^{(5,7,8)}\) reported in the literature. The figure also shows that, as the concentration of GdO\(_{1.5}\) increased, lattice parameter of GdO\(_{1.5}\)-CeO\(_2\) system increased in the range of 0 to 40 % GdO\(_{1.5}\) and decreased in the range of 60 to 90 % GdO\(_{1.5}\). Compared to YO\(_1\),CeO\(_2\) system, the change in the lattice parameter in GdO\(_{1.5}\)-CeO\(_2\) system was very small. In Figure 4, the lattice parameter continuously increased in NdO\(_1\),CeO\(_2\) system up to 75 % NdO\(_1\),CeO\(_2\) where the solubility limit had reached and the lattice parameter was constant in the range of 75 to 80 % NdO\(_1\),CeO\(_2\). The two different straight lines corresponded to one region where there was no satellite peaks and other region where there were satellite peaks. It seems that Vegard's law was obeyed in these regions with different slope. The values of lattice parameter for NdO\(_1\),CeO\(_2\) system agreed\(^{(9)}\) fairly well with those reported by other researchers\(^{(9,10)}\).

The change in lattice parameter could be interpreted by the difference in ionic radius of rare earth elements. In eightfold coordination, the ionic radius\(^{(1)}\) of Y\(^{3+}\) is 0.1013 nm. It is 0.106 nm for Gd\(^{3+}\) and 0.112 nm for Nd\(^{3+}\). Although the ionic radius of Ce\(^{4+}\) in eightfold coordination is 0.097 nm and is the smallest among the cations shown in this paper, the size of lattice parameter is complicated because oxygen vacancy could be created when trivalent cation is added into CeO\(_2\). For example in the case of YO\(_1\),CeO\(_2\) the quasi-chemical reaction is:

\[
\text{CeO}_2 + 2\text{Y}^{3+} \rightarrow 2\text{Y}^{3+} + 3\text{O}^{2-} + \text{V}^{2+}
\] (1)

The vacancy in the lattice such as shown in Eq. (1) would lead to smaller lattice parameter. The effect of vacancy on the size of lattice parameter would be the same in YO\(_1\),CeO\(_2\), GdO\(_1\),CeO\(_2\) and NdO\(_1\),CeO\(_2\) systems, if we compare it at the same cation % of additives. On the other hand the existence of additives with larger ionic size would expand the lattice parameter. Consequently for the NdO\(_1\),CeO\(_2\) system where the size of Nd\(^{3+}\) is the largest, the lattice parameter expands at every concentration shown in Fig. 4. For the case of GdO\(_1\),CeO\(_2\) where the size of Gd\(^{3+}\) is smaller than that of Nd\(^{3+}\), expansion effect of Gd\(^{3+}\) has almost canceled out with the shrinking effect of oxygen vacancy and the lattice parameter was almost constant as the concentration of Gd\(^{3+}\) increased. For the case of YO\(_1\),CeO\(_2\) where the size of Y\(^{3+}\) is almost the same as Ce\(^{4+}\), the lattice parameter shrinks at every concentration of Y\(^{3+}\) as shown in Fig. 3.

4. OXYGEN DIFFUSION COEFFICIENT

Diffusion of oxygen ions in metal oxide system involves the movement of negative ions (O\(^{2-}\)) through the barriers formed by positive ions. Since it is natural to assume that the closer the distance between positive ions is, the higher the barriers for negative ions become, the diffusion coefficient of oxygen in these oxide systems might be influenced by the size of lattice parameter.

![Figure 5. Oxygen diffusion coefficients in CeO\(_2\) solid solutions. Reprinted from ref. 12 with permission from Society of Inorganic Materials, Japan.](image)

The oxygen diffusion coefficients in CeO\(_2\) solid solutions are summarized\(^{(12)}\) in Figure 5. The figure includes the results of many researchers\(^{(13,17)}\). The figure shows that the oxygen diffusion coefficient depends strongly on temperature, because it is a thermally activated process. It also shows that the oxygen diffusion coefficient varied in wide range. We can examine the hypothesis discussed in the previous paragraph: the relationship between oxygen diffusion coefficient and lattice parameter. The temperature of 900°C (T\(^{-1}\) = 8.53 x 10\(^{-4}\) K\(^{-1}\)) was
chosen and the oxygen diffusion coefficients \( (D_{\text{oxy}}) \) at this temperature were taken at different concentration of additives. Corresponding lattice parameters were determined from Figures 3 and 4. Then, \( \log D_{\text{oxy}} \) is plotted in Figure 6 as a function of lattice parameter. From the figure it can be said that there was no clear correlation between \( \log D_{\text{oxy}} \) and the lattice parameter. The lattice parameter of pure CeO\(_2\) was about 0.5411 nm. The diffusion coefficient in pure CeO\(_2\) is the lowest as seen in Figure 5. Therefore, as the lattice parameter increased or decreased from 0.5411 nm, the diffusion coefficient always increased. This implies that the size of barriers for diffusion was not the decisive factor for the magnitude of oxygen diffusion coefficient.

\[
\log D_{\text{oxy}} = C_v D_v \tag{2}
\]

where \( C_v \) is the concentration of oxygen vacancy and \( D_v \) is the diffusion coefficient of oxygen vacancy. Since the additives such as Y\(^{3+}\), Gd\(^{3+}\) and Nd\(^{3+}\) create vacancy through quasi-chemical reaction, from the equation (1) we obtain \( 2[V_{o^-}] = [Y_{Ce^+}] \). We also obtain from the definition that \( [V_{o^-}] = C_v \). Therefore, we have

\[
D_{\text{oxy}} \propto [Y_{Ce^+}] D_v \propto [Y_{Ce^+}] \tag{3}
\]

and in general

\[
D_{\text{oxy}} \propto [M] \tag{4}
\]

where \([M]\) is the concentration of trivalent cation \( M \). Consequently, \( \log D_{\text{oxy}} \) could be proportional to \( \log [M] \) with the slope of unity. Using the data shown in Figure 5, \( D_{\text{oxy}} \) at various concentration of \( M \) can be obtained. For example, in the case of 10 % YO\(_{1.5}\)-CeO\(_2\),

\[
[M] = 0.10
\]

\( \log D_{\text{oxy}} \) at \( T^{-1} = 8.53 \times 10^{-4} \text{ K}^{-1} \) is -11.40. For pure CeO\(_2\), we used the concentration of trivalent impurities existed in the sample. In the case of CeO\(_2\) studied by Kamiya \etal \(^{17}\) they were Al and Fe. The results\(^{3} \) are shown in Figure 7 where \( D = D_{\text{oxy}} \). From the figure it can be said that there is a clear correlation between \( \log D \) and \( \log [M] \): the equation (4) is obeyed by the oxygen diffusion coefficients in the ceria-based solid solutions.

\[\text{Figure 6.} \quad \text{Oxygen diffusion coefficients in CeO}_2 \quad \text{and CeO}_2\text{-based solid solutions at 900°C as a function of lattice parameter.}\]

In general, oxygen diffusion coefficient \( (D_{\text{oxy}}) \) is written\(^{16}\) as

\[
D_{\text{oxy}} = C_v D_v \tag{2}
\]

\[\text{Figure 7.} \quad \text{Plot of } \log D \text{ vs. } \log [M] \text{ in this figure } D = D_{\text{oxy}}. \text{ Reprinted from ref. 3 with permission from Trans Tech Publications.}\]

The results in Figure 6 and 7 indicate that oxygen diffusion coefficients in CeO\(_2\) solid solutions do not depend on the size of lattice. Instead they depend on the concentration of aliovalent additives.

5. CONCLUSIONS

In three ceria-based solid solutions (YO\(_{1.5}\)-CeO\(_2\), GdO\(_{1.5}\)-CeO\(_2\), and NdO\(_{1.5}\)-CeO\(_2\)), the crystal structure at low concentration of trivalent cations is in fluorite structure and at higher concentration of cations, it is in rare earth C-type structure. As the concentration of additives increases, the lattice parameter for YO\(_{1.5}\)-CeO\(_2\) decreases continuously, and it increases for NdO\(_{1.5}\)-CeO\(_2\). For the case of GdO\(_{1.5}\)-CeO\(_2\), it was almost constant. Oxygen diffusion does not depend on
the size of crystal lattice. Instead it depends on the concentration of trivalent cation additives.

*In this review paper the expressions such as YO_{1.5}, GdO_{1.5} and NdO_{1.5} were used instead of Y_2O_3, Gd_2O_3 and Nd_2O_3, because in these expressions we can easily find out what is the cation % in the complex oxide system. For example, in the case of 10 % YO_{1.5}-CeO_2, cation % of Y is 10 %.

References


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