THERMODYNAMIC CONSIDERATIONS ON CERIA-BASED FLUORITE-TYPE OXIDES WITH EMPHASIS ON MISCIBILITY GAP, ELECTRON CONCENTRATION AND PROTON SOLUBILITY

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ABSTRACT

Experimentally observed interesting features of the ZrO$_2$-CeO$_2$-YO$_{1.5}$ system have been clarified as follows: miscibility gap was observed in (Zr$_{1-x}$Ce$_x$)$_2$YO$_{19}$ only at 1273 K by Synchrotron XRD; electron conductivity was enhanced in the middle of the composition region; the proton solubility at 973-1023 K exhibited increase with the cerium content with the maximum around $x = 0.8$. These features have been analyzed with the thermodynamic modeling of the CeO$_2$ containing fluorite phases in terms of the interaction parameters in the related binary subsystems. The miscibility gap was taken into account in terms of the positive interaction parameters between ZrO$_2$ and CeO$_2$, whereas the large negative values were obtained between ZrO$_2$ and CeO$_{1.5}$ in our previous work on the ZrO$_2$-based ceramics. These parameters can successfully reproduce the high concentration of Ce$^{3+}$ in the middle of the composition. There can be also found a correlation between the proton solubility and the chemical potential value of YO$_{1.5}$; that is, the proton solubility has a similar composition dependence to that of the activity of YO$_{1.5}$. This is reasonable from the equivalent chemical reaction: YO$_{1.5}$ + 0.5 H$_2$O = YOOH. These macroscopic features have been also discussed in terms of the microscopic defect characteristics.

INTRODUCTION

Ceria and ceria-based ceramics have been investigated for a long time as electrolyte or...
electrode related materials in solid oxide fuel cells (1,2). As an electrolyte, its high electron conductivity makes the conversion efficiency low and therefore makes it inappropriate as electrolyte. On the other hand, the presence of electrons makes it attractive to use ceria as one of electrode materials in both cathode and anode. We have also made a series of investigations on those electrochemical and physicochemical properties of ceria-based materials which seem to be closely related to anode and cathode electrode activities (3-7); for example, the following were investigated: anode characteristics on ceria coated YSZ (3); oxide ion diffusion coefficients and surface reaction rate (4), electron conductivity (5), proton solubility in the \((Zr_{1-x}Ce_x)Y_{0.5}O_{1.9}\) solid solutions (6), and proton solubility in doped ceria (7). These results make it clear that electronic conductivity alone cannot explain the electrochemical behavior associated with the presence of ceria. On the other hand, the thermodynamic properties of \(ZrO_2\)-based ceramics have been successfully represented in terms of the simple sub-regular solution model (8,9). In the present investigation, the electron concentration and the proton solubility have been used in the thermodynamic modeling for ceria-based fluorite phase to obtain the systematic understanding of the electrochemically related characteristics of ceria-based ceramics.

**THERMODYNAMIC REPRESENTATION OF FLUORITE PHASE**

The subregular solution model (in other words, the Redlich-Kister-Maggianu formalism) has been adopted according to the previous work on the \(ZrO_2\)-based ceramics. That is, the following equations are used to represent the Gibbs energy of the fluorite phase which consists of several oxide components with the respective concentrations, \(x_i\).

\[
G(\text{fluorite}) = \sum x_i \{G^\circ(X_i, \text{fluorite}) + RT \ln x_i\} + \sum_{i\neq j} x_i x_j \{A^0_{ij} + A^1_{ij}(x_i - x_j)\} \tag{1}
\]

\[
G^\circ(X_i, \text{fluorite}) = a + b T \quad (X_i = \text{ZrO}_2, \text{CeO}_2, \text{CeO}_{1.5}, \text{YO}_{1.5}) \tag{2}
\]

where \(G^\circ(X_i, \text{fluorite})\) is the lattice stability of a compound \(X_i\) and \(A^0_{ij}, A^1_{ij}\) are the first and the second interaction parameters in the Redlich-Kister equation for the \(i\)-\(j\) binary subsystem.

In the \(ZrO_2\)-based ceramics (8), the interaction parameters were determined by considering the following:

1) Experimentally determined thermodynamic properties (EMF etc).
2) Phase diagram information
3) Correlation based on the ionic properties.

For ceria-based ceramics, a similar approach can be adopted. As experimental information, the thermogravimetric results are available for the \(\text{CeO}_2-\text{CeO}_{1.5}\) system and the \(\text{Gd-}, \text{Sm-}, \text{and Y-doped systems. Recently, the miscibility gap was observed in the}\) \(\text{ZrO}_2-\text{CeO}_2-\text{YO}_{1.5}\) system. From those information, the interaction parameters have been optimized (9).
Table 1 Interaction parameters derived in the present and previous investigations\(^{(8,9)}\)
(a) Binary interaction parameters of the fluorite type phases.

| Binary system          | $A_{ii}^0$ (J/mol) | $A_{ii}^1$ (J/K mol) | $A_{ij}^0$ (J/mol) | $A_{ij}^1$ (J/K mol) | Remarks                  |
|------------------------|--------------------|----------------------|--------------------|----------------------|--------------------------|
| ZrO$_2$-YO$_{1.5}$     | -65,000            | 0                    | -25,000            | 0                    | Based on EMF data        |
| ZrO$_2$-CeO$_2$         | 6000               | 0                    | -3000              | 0                    | Miscibility gap data      |
| ZrO$_2$-CeO$_{1.5}$    | -53,000            | 0                    | 23,000             | 0                    | Phase diagram data        |
| CeO$_2$-YO$_{1.5}$     | 28,000             | 25.5                 | 18,000             | 4.4                  | Estimate                 |
| CeO$_2$-CeO$_{1.5}$    | -1,800             | 25.5                 | 30,700             | 4.4                  | TG etc.                  |
| CeO$_{1.5}$-YO$_{1.5}$ | -30,000            | 0                    | 30,000             | 0                    | Estimate                 |

(b) Lattice stability of the fluorite phases against the most stable phase

| Compounds | $a$ (kJ mol$^{-1}$) | $b$ (J mol$^{-1}$ K$^{-1}$) | The most stable phase |
|-----------|--------------------|-----------------------------|-----------------------|
| ZrO$_2$   | 21.4               | 10.69                       | Monoclinic            |
| YO$_{1.5}$| 7.5                | 0                           | C-type                |

The thermodynamic properties of the CeO$_2$-based fluorite phase have been well investigated with a focus on the redox behavior of Ce$^{4+}$/Ce$^{3+}\(^{(2,10)}\)$. One of the most important features in the CeO$_2$ fluorite phase is the phase separation at low temperatures. This is represented by the positive interaction parameters between CeO$_2$ and CeO$_{1.5}$. With increasing temperature, the tendency towards phase separation becomes weak and this is represented by the negative interaction parameters. These features suggest that the excess entropy is large as indicated in Table 1.

The thermogravimetric results\(^{(11,12,13)}\) were used to optimize the interaction parameters between CeO$_2$ and REO$_{1.5}$. Here, the entropy term was assumed to have the same values as those in the CeO$_2$-CeO$_{1.5}$ system.

Fig. 1 (a) The lattice constants of (Zr$_{1-x}$Ce$_x$)$_{0.8}$Y$_{0.2}$O$_{1.9}$ solid solutions annealed at 1273 K\(^{(16)}\). Calculated values were derived from the tie-line composition and the additive rule for the lattice constants. (b) Calculated miscibility gap and tie lines in the ZrO$_2$-CeO$_2$-YO$_{1.5}$ system.
Although earlier investigations\(^\text{(14,15)}\) indicated that the miscibility gap appears in the 
ZrO\(_2\)-CeO\(_2\)-YO\(_{1.5}\) system even at high temperatures around 1600 °C, our recent 
investigation has clarified that the miscibility gap appears only at 1000 °C \(^\text{(16)}\). Figure 1 
shows the observed lattice constants. In the CeO\(_2\)-rich region, apparently two fluorite 
phases were identified. To reproduce these behaviors, the interaction parameters were 
optimized for the ZrO\(_2\)-CeO\(_2\) and CeO\(_2\)-YO\(_{1.5}\) subsystems, whereas those parameters for 
the ZrO\(_2\)-CeO\(_{1.5}\) subsystem were already obtained in our previous investigation on the 
ZrO\(_2\)-based ceramics.

**COMPARISON BETWEEN YSZ AND YDC**

In many cases, doped ceria is compared with yttria stabilized zirconia (YSZ). Here, the 
thermodynamic and related properties are compared between YSZ and yttria doped 
ceria(YDC). Figure 2 shows the total Gibbs energy of the fluorite phase in the ZrO\(_2\)-YO\(_{1.5}\) 
and the CeO\(_2\)-YO\(_{1.5}\) systems. At 1273 K, the monoclinic ZrO\(_2\) is more stable than the 
fluorite type so that the Gibbs energy of the fluorite ZrO\(_2\) is positive. On adding the YO\(_{1.5}\) 
component, the Gibbs energy decreases rapidly, indicating that the fluorite phase is 
stabilized appreciably by the YO\(_{1.5}\) component. In the CeO\(_2\)-YO\(_{1.5}\) system on the other hand, 
the fluorite phase is the most stable phase in the CeO\(_2\)-rich region and the Gibbs energy 
does not change sensitively on the composition of the YO\(_{1.5}\) component.

These differences also appear in the magnitude and the composition dependence of 
chemical potential of the YO\(_{1.5}\) component as shown in Fig. 2. At \(x(\text{YO}_{1.5})=0.2\), the 
chemical potential of YO\(_{1.5}\) exhibits about 50kJ/mol difference between YSZ and YDC. 
This is extraordinary large. From the microscopic point of view, this difference can be

![Fig. 2 The total Gibbs energy of the fluorite phase and the chemical potential of YO\(_{1.5}\) in the ZrO\(_2\)-YO\(_{1.5}\) and CeO\(_2\)-YO\(_{1.5}\) systems at 1273 K.](image_url)
attributed to the recently clarified facts(17) on the difference in the location of the oxide ion vacancies. In YSZ, the oxide ion vacancies tend to locate around the Zr$^{4+}$ ions. Since the monoclinic ZrO$_2$ has the 7 coordinated oxide ions around Zr$^{4+}$, it can be said that the Zr$^{4+}$ ions are slightly small to have the 8 coordinated oxide ions and this is the reason for the instability of the fluorite ZrO$_2$ against the monoclinic ZrO$_2$. When the YO$_{1.5}$ component is added and the vacancies are generated around the Zr$^{4+}$ ions, the Zr$^{4+}$ ions have the 7 or less coordinates even in the fluorite structure. This is the defect chemical explanation for the strong stabilization of YSZ. On the other hand, the Ce$^{4+}$ ions are large enough for the fluorite structure. This leads to the situation that the vacancies do not need to be created around Ce$^{4+}$. Thus, the vacancies are formed around Y$^{3+}$ in YDC and do not give rise to any significant energetic change around the Ce$^{4+}$ ions.

**SHIFT OF REDOX EQUILIBRIUM BETWEEN Ce$^{3+}$/Ce$^{4+}$**

The redox equilibrium between Ce$^{3+}$/Ce$^{4+}$ can be expressed in terms of the chemical potentials of CeO$_2$ and CeO$_{1.5}$ according to the following equations:

\[
\begin{align*}
\text{CeO}_2\text{(in fluorite)} & = \text{CeO}_{1.5}\text{(in fluorite)} + 0.25 \text{O}_2\text{(g)} \quad (3) \\
\mu(\text{CeO}_2) & = \mu(\text{CeO}_{1.5}) + 0.25\mu(\text{O}_2) \quad (4)
\end{align*}
\]

In phase diagram calculations using the interaction parameters, the chemical potentials of CeO$_2$ and CeO$_{1.5}$ can be calculated using the Redlich-Kister-Maggianu formalism(8,9) at selected compositions in any system containing CeO$_2$ and CeO$_{1.5}$ as components. Figure 3 compares these chemical potentials as a function of the concentration of the cerium trivalent ions among the cerium ions in CeO$_{2-d}$, CeO$_{2-d}$YO$_{1.5}$O$_{0.2}$, and CeO$_{2-d}$ZrO$_{2}$O$_{0.2}$. In CeO$_{2-d}$, the tendency towards phase separation can be seen in the flat behavior of the

![Graph](image-url)  

**Fig. 3** The chemical potentials of CeO$_2$ and CeO$_{1.5}$ in CeO$_{2-d}$, CeO$_{2-d}$YO$_{1.5}$O$_{0.2}$, and CeO$_{2-d}$ZrO$_{2}$O$_{0.2}$. The smaller difference between two values indicates the larger shift of the redox equilibrium to the oxidative side.

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chemical potential of CeO$_2$. In the 20\% YO$_{1.5}$ or ZrO$_2$ doping systems, the chemical potential of CeO$_2$ remains flat in the CeO$_2$-rich region and has larger values in the CeO$_{1.5}$-rich region, while that of CeO$_{1.5}$ decreases over a wide range of concentration. Both behaviors make contribution to shift the redox oxygen potential to the oxidative side. In other words, the concentration of the trivalent ions increases on forming solid solutions with YO$_{1.5}$ or ZrO$_2$. This effect appears more significantly in the ZrO$_2$ doping than in the YO$_{1.5}$ doping system.

From the macroscopic point of view, the above behavior can be explained as follows: 1) The interaction parameters in the ZrO$_2$-CeO$_2$ subsystem are positive, whereas those in the ZrO$_2$-CeO$_{1.5}$ subsystem are strongly negative. The former is consistent with the fact that the ZrO$_2$-CeO$_2$-YO$_{1.5}$ system has the miscibility gap in the CeO$_2$-rich corner. The latter is similar to the ZrO$_2$-YO$_{1.5}$ system shown in Fig. 2. 2) A similar behavior of the interaction parameters can be seen in the CeO$_2$-YO$_{1.5}$ system and in the CeO$_{1.5}$-YO$_{1.5}$ system. Numerical interaction parameters given in Table 1 indicate that although the CeO$_2$-YO$_{1.5}$ and CeO$_{1.5}$-YO$_{1.5}$ systems have a similar trend to the ZrO$_2$-analogous systems, the magnitude is about half. This directly affects the magnitude of the shift of the redox equilibria. 3) In the ZrO$_2$-CeO$_2$-YO$_{1.5}$ system, the shift can be calculated using those interaction parameters determined from the thermogravimetric results(9). These properties can be directly compared with the electron conductivity in the solid solutions. Figure 4 compares the calculated concentration of combined cerium trivalent and cerium tetravalent ions with the observed electron conductivity at 1273 K. The present set of interaction parameters can successfully reproduce the composition dependence of electron conductivity in terms of the concentration of cerium trivalent ions which produce electron carriers and the concentration of cerium tetravalent ions which should be needed for electrons to hop to the adjacent cerium sites. Optimization on interaction parameters may improve the agreement between experiment and calculation.

![Graph](image_url)

Fig. 4 The calculated contribution to the electron conductivity, that is, log (n[Ce$^{3+}$] n[Ce$^{4+}$]), which should be compared with the composition dependent electron conductivity for (Zr$_{1-x}$Ce$_x$)$_8$(Y)$_{0.2}$O$_{1.9}$d at 1273 K and $p$(O$_2$)$=10^{-4}$ atm.
From the microscopic point of view, the following can be pointed out by considering the defects distribution in the fluorite structure:

1) In CeO$_2$, the oxide ion vacancies tend to locate around the cerium trivalent ions particularly at low temperatures, because the interaction between CeO$_2$ and CeO$_{1.5}$ is small.

2) When the cerium trivalent ions are formed in the ZrO$_2$-CeO$_2$ system, the associated oxide ion vacancies will be formed in the vicinity of Zr$^{4+}$, not of Ce$^{3+}$. In other words, the vacancies formed around the cerium trivalent ions tend to migrate to the vicinity of Zr$^{4+}$ to stabilize the ZrO$_2$ component and the CeO$_{1.5}$ component. This corresponds to the strong interaction between ZrO$_2$ and CeO$_{1.5}$ and significant lowering of the chemical potential of CeO$_{1.5}$.

3) The strong interaction between CeO$_{1.5}$ and YO$_{1.5}$ suggests that the oxide ion vacancies around the cerium trivalent ions move to the vicinity of Y$^{3+}$ ions to stabilize both CeO$_{1.5}$ and YO$_{1.5}$.

**PROTON SOLUBILITY**

Recently we have measured the proton solubility in (Zr$_{1-x}$Ce$_x$)$_{0.8}$Y$_{0.2}$O$_{1.9}$ solid solutions (6) in a similar technique used for the rare earth doped ceria (7). In Fig. 5, the observed values are plotted against the cerium composition. The logarithmic proton solubility increases linearly with the cerium composition and in the CeO$_2$-rich region, the solubility has the maximum around $x$(Ce) = 0.8.

![Fig. 5 Observed proton solubility in (Zr$_{1-x}$Ce$_x$)$_{0.8}$Y$_{0.2}$O$_{1.9}$ solid solution around 1000 K under a selected partial pressure of water vapor. The calculated values are derived from the calculated chemical potential of YO$_{1.5}$ in solid solutions under an approximation for the Raoult law for the chemical potential of YOOH. The dashed line was obtained by considering the volume expansion effect of dissolution of water.](image-url)
This composition dependence is interesting from the behavior of chemical potentials derived for the solid solutions. Among the chemical potentials of the components, that of YO$_{1.5}$ shows a very similar dependence to that of the proton solubility. This can be reasonably taken into account from the following chemical reaction:

\[ \text{YO}_{1.5} \text{(in fluorite)} + 0.5 \text{H}_2\text{O(g)} = \text{YOOH(in fluorite)} \]  

\[ \mu(\text{YO}_{1.5}) + 0.5 \{\mu^o(\text{H}_2\text{O}) + RT \ln p(\text{H}_2\text{O})\} = \mu^o(\text{YOOH}) + RT \ln c(\text{YOOH}) \]  

where Henry's law is adopted in the chemical potential of YOOH, and \(\mu^o(\text{YOOH})\) is the Henrian standard value. As the first order of approximation,

\[ \mu^o(\text{YOOH}) = \mu^o(\text{YOOH}) \]  

can be adopted. Here, \(\mu^o(\text{YOOH})\) is the standard state for the bulk YOOH; in other words, the Raoultian standard value. This value can be evaluated from the known Gibbs energy values for Y$_2$O$_3$ and Y(OH)$_3$ with the same stabilization energy as LaOOH and FeOOH. Since other terms in Eq.(6) are all known, the concentration of YOOH namely H$^+$ can be calculated as given as solid line in Fig. 5. A dashed line was derived after correction for volume change: The molar volume of YOOH is about 25.53 cm$^3$/mol, whereas the solid solutions change from 20.5 cm$^3$/mol for (Zr$_{0.8}$Y$_{2})_{0.9}$ to 23.4 cm$^3$/mol for (Ce$_{0.8}$Y$_{2})_{0.9}$. This indicates that on the dissolution of water, the volume will expand. The Henrian standard value may be adjusted for this size effect.

The calculated solubility based on the Raoultian standard shows essentially the same magnitude as the observed values. This confirms the following:

1) We implicitly assumed that protons exist as OH' group in lattice and OH' is located around the Y$^{3+}$ ions. In other words, Y$^{3+}$, not Zr$^{4+}$, stabilizes protons in oxides. Our earlier investigation revealed that the proton solubility depends on dopants (7). In the present case, the concentration of Ce$^{3+}$ is calculated to be small compared with that of Y$^{3+}$ so that the consideration of YOOH alone seems reasonable.

2) Although the concentration of Y$^{3+}$ is the same between YSZ and YDC, the proton solubility is different. This is due to the large difference in the chemical potential of YO$_{1.5}$ shown in Fig. 2. In YSZ, the oxide ion vacancies are located around the Zr$^{4+}$ ions and not around the Y$^{3+}$ ions so that those Y$^{3+}$ ions which are already surrounded by oxide ions can not provide room for receiving the hydroxide ion and proton. Water can be dissolved into YSZ through the vacancy sites near to the Zr$^{4+}$ ions. The dissolved proton may migrate to the vicinity of the Y$^{3+}$ ions. In YDC, the oxide ion vacancies are formed around the Y$^{3+}$ ions so that water can be dissolved directly into those sites near to the Y$^{3+}$ ions. As a result, the hydroxide ions are formed near the Y$^{3+}$ ions, which is similar to the ionic configuration in the bulk YOOH.

These considerations along with the defect chemistry help in understanding the observed effects of water on the oxygen isotope exchange reaction rate of the fluorite phase; that is, a small amount of water can enhance the isotope exchange reaction significantly on YSZ and also to some extent on YDC (18).

In many cathode and anode reactions, doped ceria exhibits interesting behavior. It seems that some of those properties can be interpreted in terms of the effects caused by water.
THERMODYNAMIC STABILITY OF CERIA-BASED CERAMICS

With the lowering of the operation temperature of SOFCs, the reactivity of the basic cell components with water vapor and carbon dioxide becomes crucial. The YO\textsubscript{0.5} component in YSZ is well stabilized so that essentially no problems arise by lowering temperature except for the formation of Y(OH)\textsubscript{3} in PSZ (partially stabilized zirconia) under the hydro-thermal condition. On the other hand, the YO\textsubscript{1.5} component is not well stabilized as shown in Fig. 2. Furthermore, there can be seen some tendency that the rare earth oxide component in CeO\textsubscript{2} becomes less stabilized by lowering temperature. This may cause the following:

1) The solubility of the rare earth oxide component in CeO\textsubscript{2} decreases rapidly with decreasing temperature.
2) This suggests that the segregation of the rare earth oxide component may occur along grain boundaries after thermal cycles.
3) Since the water solubility in doped ceria is rather high, there is some possibility that the water in the fluorite phase may assist such segregation of rare earth oxide along grain boundaries. Actually, the sample annealed in the humidified atmosphere at a high temperature and kept at room temperature exhibited changes in grain boundaries.
4) There seems much more chance for the YO\textsubscript{1.5} component to be precipitated as Y(OH)\textsubscript{3} in YDC at low temperatures than in YSZ.

CONCLUSIONS

An attempt was made to interpret changes in concentration of electrons and in proton solubility in the CeO\textsubscript{2}-based fluorite phase in terms of the macroscopic thermodynamic properties derived from the interaction parameters and of the microscopic defect chemical features. The fundamental features can be satisfactorily taken into account in the present approach. We therefore hope to investigate further the details of the correlation between the macroscopic thermodynamic properties and the defect chemical properties and to provide the fundamentals for optimization of the utilization of the CeO\textsubscript{2}-based ceramics as electrode and related materials in solid oxide fuel cells.

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