Oxygen release behavior of metastable tetragonal \( t'_\text{meta}-(\text{Ce}_{0.5}\text{Zr}_{0.5})\text{O}_2 \) phases prepared by reduction and successive oxidation of \( t' \) phase

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Abstract

Tetragonal CaF\(_2\)-related-type \( t'-(\text{Ce}_{0.5}\text{Zr}_{0.5})\text{O}_2 \) phase was reduced at 773 K \( \leq T_{\text{red}} \leq 1073 \) K to prepare precursors with various oxygen compositions: \( \text{Ce}_2\text{Zr}_2\text{O}_7\text{+}\_\_ \) \((0.111 < \delta < 0.379)\). Metastable tetragonal \( t'_\text{meta}-(\text{Ce}_{0.5}\text{Zr}_{0.5})\text{O}_2 \) phases were prepared by oxidizing in \( \text{O}_2 \) at 873 K the precursors, and subjected to evolved oxygen gas analysis by heating the samples at a constant rate. When the precursor was prepared at \( T_{\text{red}} = 773 \) K, i.e. \( \delta = 0.379 \), the oxygen release behavior of the tetragonal phase agreed approximately with that of the \( t' \). For \( \delta < 0.29 \), distinct features of the \( t'_\text{meta}-(\text{Ce}_{0.5}\text{Zr}_{0.5})\text{O}_2 \) appeared in the XRD results and Raman spectra. The temperature exhibiting the maximum release rate of oxygen from the \( t'_\text{meta} \) became lower with decreasing the \( \delta \) value. It could be concluded that the thermodynamic behavior of the \( t'_\text{meta} \) is related closely to the precursor composition and becomes more unstable with decrease in the \( \delta \) value. The \( t' \) and \( t'_\text{meta} \) phases with disordered arrangement of Ce and Zr ions may belong to the same space group; nevertheless, difference in the random arrays of the Ce and Zr ions was suggested on the basis of the present experimental results. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

In the intermediate composition range of the equilibrium phase diagram in the \( \text{CeO}_2-\text{ZrO}_2 \) system, no compound exists except for cubic CaF\(_2\)-type (Ce, Zr\(_{1-x}\))O\(_2\) phases over 1823 K [1,2]. At intermediate temperatures, monoclinic ZrO\(_2\)-based and cubic CeO\(_2\)-based phases below 1323 K and tetragonal ZrO\(_2\)-based and cubic CeO\(_2\)-based phases above 1323 K coexist, respectively. In the range of \( x = 0.2-0.7 \), when the cubic CaF\(_2\)-type (Ce, Zr\(_{1-x}\))O\(_2\) phase is cooled in the furnace, in spite of its low cooling rate [3,4], a tetragonal \( t' \) form maintaining random distribution of Ce and Zr ions could appear through a cation diffusionless phase transition without the phase separation [2]; it has been disputed whether the \( t' \) form is a metastable phase [2,5]. When the pyrochlore-type Ce\(_2\)Zr\(_2\)O\(_7\)-\_\_ phase possessing arrays of Ce and Zr ions, respectively, in the \((110)\) direction is oxidized at a low temperature, e.g. 873 K, oxygen is intercalated leaving the ordered arrangement of Ce and Zr ions in the resulting phase [3,6–8]; the crystallographic character of the metastable \( \kappa \)-CeZrO\(_4\) phase obtained has been recently studied in detail [9].

The appearance of the metastable \( \kappa \) phases may be understood phenomenally from the schematic diagram of the phase transformation of Ce/Zr composition ratio \( = 1 \), as shown in Fig. 1. Recently, three of the authors (T.O., H.K., S.O.-Y.-M.) [8] prepared the precursors, Ce\(_2\)Zr\(_2\)O\(_7\)-\_\_ with various \( \delta \) values by reducing the \( t' \) phase at various temperature: 873 K \( \leq T_{\text{red}} \leq 1573 \) K; the mixing-state, i.e. ordering level of Ce and Zr ions may differ among the precursors. As the \( \delta \) value was decreased, the precursor became a pyrochlore-type, and therefore the final phase obtained by reoxidation was the \( \kappa \)-CeZrO\(_4\). When the \( \delta \) value was large, i.e. the reduction rate was small, the final phase was the \( t' \) phase, as expected. For an intermediate reduction rate, i.e. \( \delta = 0.113 \), the final phase obtained by reoxidation was a novel metastable tetragonal (Ce\(_0.5\)Zr\(_{0.5}\))O\(_2\) phase, which possessed a similar disordered arrangement of cations to the \( t' \) phase but might have a slightly different coordinate of oxygen from the \( t' \); the novel tetragonal phase was named \( t'_\text{meta}-(\text{Ce}_{0.5}\text{Zr}_{0.5})\text{O}_2 \) [8,10]. When heating the \( t'_\text{meta} \) in \( \text{O}_2 \) gas over 1273 K, the \( t'_\text{meta} \) phase became the \( t' \) phase [10].

Investigation on metastable phases must become increasingly important because metastable states may make it possible to attain various physical properties of materials without change in the chemical composition. As the \( \delta \) value of the precursors, Ce\(_2\)Zr\(_2\)O\(_7\)-\_\_ decreases, the Raman band around 524 cm\(^{-1}\) observed for the \( t' \) appeared to...
stable tetragonal $t'_{\text{meta}}$(Ce$_{0.5}$Zr$_{0.5}$)O$_2$ phases obtained by the reoxidation was studied by using the same apparatus and a similar technique. The oxygen analyzer developed by one of the authors [11–13] enables measurements with much higher sensitivity and therefore uses smaller amounts of samples than such conventional technique as gas chromatography–mass spectrometry or mass thermobalances. Details of experimental principle and techniques of the oxygen analyzer have been described in earlier papers [11,14]. In this paper, procedures for obtaining the rate and amount of oxygen released from a sample are briefly stated.

The oxygen analyzer includes an electrochemical oxygen pump: Pt, air/ZrO$_2$/(+CaO) electrolyte/Ar +1%H$_2$ gases, Pt. The potentiostatic operation with four leads was carried out so that the emf, $E$, between the leads for emf measurements could be set to $-1.3$ V; the oxygen chemical potential at the solid electrolyte/Ar interface ($x = L$), $\mu(O_2)$, was maintained at a constant value. The corresponding oxygen partial pressure, $P(O_2)$, was evaluated to be $7.9 \times 10^{-26} \times 101325$ Pa using the equation [15]

$$E = (RT/4F)\ln\left\{P(O_2)/((0.21 \times P^*)\right\},$$

where $R$ is the gas constant $(8.31441 \text{ J mol}^{-1}\text{k}^{-1})$, $T$ the temperature of the electrochemical oxygen pump $(1073 \text{ K})$, $F$ the Faraday’s constant $(96484.56 \text{ C mol}^{-1})$, and $P^*$ is the 101325 Pa.

Because the oxygen in the closed system was electrochemically evacuated through the electrolyte, the $P(H_2)/P(H_2)$ ratio of the circulating Ar +1% H$_2$ gas mixtures became virtually a constant value, i.e. $4.2 \times 10^{-4}$, and the electric current, $I$, decreased to the base-current, $I_w(t)$. A small change in $I_w(t)$ with time could be expressed by a function, $I_w(t) = \exp(-a(t+b) + c$. After confirming the base current, $I_w(t)$, the EGA analysis was started by heating the sample chamber at a constant rate of $R = 2$ K min$^{-1}$. When the oxygen is released from the sample into the system upon heating, the oxygen chemical potential in the circulating gas, $\mu(O_2)^\text{circ}$, becomes larger than $\mu(O_2)^\text{circ}$. Because the oxygen is electrochemically pumped out of the system, the electric current, $I$, is increased from $I_w(t)$. The term, $\{I - I_w(t)\}$, is attributable to the ionic component; the amount of oxygen released by the sample per second, $J_0$ (oxygen ion mol s$^{-1}$), is evaluated by the following equation

$$J_0 = (I - I_w(t))/2F$$

The total amount of oxygen, $N(0)$, in mol released by the sample in the reaction, can be evaluated from the ionic charge, $Q_\text{ion}$, by integrating $\{I - I_w(t)\}$ with $t$

$$N(0) = Q_\text{ion}/2F = (1/2F) \int \{I - I_w(t)\} \, dt = \int J_0 \, dt$$

Fig. 1. Schematic diagram of the phase transformation of cerium zirconium oxides with the Ce/Zr composition ratio $= 1$ induced by reduction and successive oxidation.

2. Experimental

2.1. EGA analysis

The oxygen content of the reduced samples, i.e. precursors must be an important factor for determining the structure and chemical properties of the reoxidized (Ce$_{0.5}$Zr$_{0.5}$)O$_2$ phase. In this study, the starting $t'$ sample was reduced in the closed-system oxygen analyzer applying EGA technique [11]; the chemical property of the metastable tetragonal $t'_{\text{meta}}$(Ce$_{0.5}$Zr$_{0.5}$)O$_2$ phases obtained by the reoxidation was studied by using the same apparatus and a similar technique. The oxygen analyzer developed by one of the authors [11–13] enables measurements with much higher sensitivity and therefore uses smaller amounts of samples than such conventional technique as gas chromatography–mass spectrometry or mass thermobalances. Details of experimental principle and techniques of the oxygen analyzer have been described in earlier papers [11,14]. In this paper, procedures for obtaining the rate and amount of oxygen released from a sample are briefly stated.

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$$N(0) = Q_\text{ion}/2F = (1/2F) \int \{I - I_w(t)\} \, dt = \int J_0 \, dt$$
2.2. Preparation of starting $t'$ phase and reduced and reoxidized samples

Starting $t'$-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$ was prepared by the conventional ceramic method as follows. Powdered raw materials CeO$_2$(Na: &lt;100 ppm, Fe: &lt;10 ppm) and ZrO$_2$(HfO$_2$: 3.8 mass%, Na: &lt;100 ppm, Fe: &lt;100 ppm), which were supplied by Santoku Kinzoku Kogyo Co., Ltd. were thoroughly mixed in a molar ratio of 1:1 using a ball mill, and pressed into 17 mm-diameter under 100 MPa. The disk was sintered in air at 1923 K for 50 h to attain a single phase with a cubic CaF$_2$-type structure; when it was cooled by cutting the electric power off in the furnace, the phase transformed to single $t'$-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$ phase.

The preparation of the $t'$-meta phases was carried out in a similar manner to that described previously [8]. In the present work, the $t'$-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$ powder of 35.44 mg, involving $1.2 \times 10^{-4}$ mol of CeO$_2$, was loaded in an alumina crucible to prepare the $t'$-meta for the EGA analysis: to enhance the reliability of the discussion on the EGA data, an identical lot of the $t'$ was used to prepare various $t'$-meta phases. Since carbon-related compounds such as CO and hydrocarbon adsorbed on the sample chamber hinder precise EGA, the sample chamber containing the alumina crucible was heated before the sample loading at 1373 K for 5 h by circulating O$_2$ gas. The system was then evacuated for a few minutes and O$_2$ gas was reintroduced. The experimental procedure after the sample loading at room temperature is illustrated in Fig. 2. After the system was evacuated, O$_2$ gas was introduced and then the sample annealed at 873 K for 5 h to control the oxygen content in it; its composition after annealing was regarded as stoichiometric (Ce$_{0.5}$Zr$_{0.5}$)O$_2$. The system was evacuated after being cooled to 373 K in O$_2$ gas, and then Ar + 1% H$_2$ gas mixture was introduced and circulated in the system. Ten hours after the potentiostatic operation with four leads, the base current, $I_{\text{red}}(t)$, became sufficiently small. The heating-reduction run for the preparation of precursor was started by heating the sample at a rate of 2 K min$^{-1}$ to the preselected temperatures $T_{\text{red}}$ of 773, 923 and 1073 K. During the heating, the sample was reduced with oxygen being released. After holding for 10 h at the $T_{\text{red}}$, in the case of $T_{\text{red}} = 923$ and 1073 K, the sample was cooled to 873 K. The system was evacuated and O$_2$ gas introduced to oxidize the precursor. In the case of $T_{\text{red}} = 773$ K, after O$_2$ gas was introduced, the sample was heated to 873 K. The composition of the $t'$-meta phase obtained agreed with its initial (Ce$_{0.5}$Zr$_{0.5}$)O$_2$; it was confirmed by the successively EGA experiment. After cooling the sample to 373 K, the system was evacuated, and then the Ar + 1% H$_2$ gas mixture was introduced and circulated in the system. Because the potentiostatic operation and EGA analysis by heating the sample to 1323 K were followed without unloading, the XRD data and Raman spectrum for the $t'$-meta were not available.

The $t'$-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$ powder of 100 mg was reduced in a similar manner at 773 K $\leq T_{\text{red}} \leq 1073$ K to prepare precursors with various oxygen compositions: Ce$_2$Zr$_2$O$_7$-$t_{2g}$. The $t'$-meta-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$ phases obtained by oxidizing in O$_2$ at 873 K the precursors were subjected to the powder X-ray diffraction analysis (Cu K$_\alpha$ radiation, using curved graphite K$_\beta$-filter, 40 kV–200 mA) (MPX18, MAC Science, Yokohama, Japan), and Raman spectroscopy. Lattice parameters were calculated applying the least squares procedure (Code RSLC) to more than seven sharp diffraction peaks among the diffractions with indices of 113, 311, 222, 004, 313, 204, 224, 115, 404, and 315. High-purity silicon powder was mixed with the samples as an internal standard. The Raman spectra were recorded by a spectrometer with a double monochromator and photomultiplier detector (JASCO, NR1100, Nihon Bunko, Tokyo, Japan) under the excitation of Ar ion laser of 514.5 nm (Innova 90C, Coherent, Santa Clara, CA).

3. Results

3.1. Preparation of metastable tetragonal phases

Fig. 3 shows the $J_0$–$T$–$t$ curves obtained when the $t'$ powders prepared from a identical lot of the $t'$-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$ disks were heated to various reducing temperatures $T_{\text{red}}$ in the closed-system oxygen analyzer. The data for $T_{\text{red}} = 1323$ K corresponds to the EGA result for the $t'$ sample. The oxygen release from it started around 673 K, and the peak, i.e. the maximum rate of oxygen release was observed around 973 K. As the temperature was further increased, the oxygen release was gradually decreased. On the $J_0$–$T$–$t$ curves, a small hump appeared at a lower temperature around 923 K than that of the large peak. The shape of the $J_0$–$T$–$t$ curve obtained in this work agreed well with that reported previously as the distinct feature for the $t'$-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$ powder [3,16]. Immediately after it reached the reducing temperature $T_{\text{red}} = 1323$ K, the oxygen release rate was changed and gradually diminished. The $J_0$–$T$–$t$ curves obtained for $T_{\text{red}} = 773$, 923 and 1073 K were consistent with that for $T_{\text{red}} = 1323$ K. Before the temperature reached the respective $T_{\text{red}}$, the $J_0$–$T$–$t$ curves for $T_{\text{red}} = 773$ and 923 K were almost coincided with that for $T_{\text{red}} = 1323$ K. For $T_{\text{red}} = 1073$ K, a hump accompanying a peak on the $J_0$–$T$–$t$ curve was observed.
Fig. 3. $J_0$–$T$–$t$ curves obtained when $t'$-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$ powder was heated at various reducing temperatures $T_{\text{red}}$ to prepare the precursor of t$_{\text{meta}}'$-(Ce$_{0.5}$Zr$_{0.5}$)O$_2$. $J_0$ indicates the oxygen evolution rate in mol of oxygen atom per sec. The reduction rate: $y = \text{Ce}^{3+}/(\text{Ce}^{3+} + \text{Ce}^{4+})$ expresses the final composition $\text{Ce}_{x}\text{Zr}_{y}O_{x+y}$; $y = 0$ and $y = 1$ correspond to the initial composition before reduction and the pyrochlore, respectively. The $\delta$ values for the $\text{Ce}_{x}\text{Zr}_{y}O_{x+y}$ precursor obtained were, respectively, $\delta = 0.379$ for $y = 0.242$ at $T_{\text{red}} = 773$ K, $\delta = 0.203$ for $y = 0.595$ at $T_{\text{red}} = 923$ K, $\delta = 0.111$ for $y = 0.778$ at $T_{\text{red}} = 1073$ K, $\delta = 0.056$ for $y = 0.889$ at $T_{\text{red}} = 1323$ K.

much like those for $T_{\text{red}} = 1323$ K. These results may support the high reliability of the present experimental technique. The $\delta$ values for the obtained $\text{Ce}_{x}\text{Zr}_{y}O_{x+y}$ precursors evaluated from the $J_0$–$T$–$t$ curves are shown in the caption of Fig. 3, together with the corresponding reduction rate. The reduction rate, $y = \text{Ce}^{3+}/(\text{Ce}^{3+} + \text{Ce}^{4+})$ may be convenient for understanding the chemical situation of the precursor. Using this notation, the precursor composition may be expressed as $\text{Ce}_{x}\text{Zr}_{y}O_{x+y}$; $y = 0$ and $y = 1$ correspond to the initial composition before reduction and the pyrochlore composition, respectively.

3.2. XRD patterns and vibrational spectra of samples

When the starting $t'$ lot was changed, the $J_0$–$T$–$t$ curves for the $t'$ powder shifted slightly along time axis, although their shape were similar. The results may have something to do with the deduction described later that the $t'$ might be a kind of the $t'_{\text{meta}}$. Although change in the oxygen release may lead to slight difference in the reduction rate, the evaluated $\delta$ and $y$ values changed monotonously with $T_{\text{red}}$. It should be emphasized that the $\delta$ value evaluated precisely in the present study is the factor affecting strongly on the properties of reoxidized phases [8].

In Fig. 4, the XRD patterns for the reoxidized samples were compared to that for starting $t'$. The diffractions with indices of 400 and 004 were clearly split. The (112) diffraction due to displacement of oxygen in the CaF$_2$-related lattice was clearly observed. Thus, the reoxidized samples were identified to have the tetragonal $t'$ or its related phase, i.e. $t'_{\text{meta}}$. Table 1 shows lattice parameters and unit cell volumes for reoxidized phases. The lattice parameters of the tetragonal phases were expressed by $a_0$ and $c_0$ based on the pseudofluorite cell, although $a_0 = a_{F} / \sqrt{2}$ and $c_0 = c_{F}$.

are actual lattice parameters for the space group of $P4_{2}/nmc$ with a dimolecular cell [17].

Fig. 5 shows the Raman spectra of the tetragonal phases. The Raman spectrum for the reoxidized phase obtained from $\delta = 0.371$ ($y = 0.258$) at $T_{\text{red}} = 773$ K was identical to that for the starting $t'$. As the $\delta$ value was decreased, the
Table 1
Structural and compositional parameters for the tetragonal (Ce0.5Zr0.5)O2 compounds obtained in this work, compared with those reported previously [8]

| Reduction temperature, $T_{\text{red}}$ (K) | Reduced CeZrO3−δ (precursor) | Reoxidized (Ce0.5Zr0.5)O2 | Crystal system | Phase | Lattice parameters$^a$ (nm) | $c_p/d_{up}$ ratio | Unit cell volume$^a$, $V$ (nm$^3$) |
|---|---|---|---|---|---|---|---|
| Present study | | | | | | | |
| 1073 | 0.710 | 0.145 | Tetragonal | $t'$ | $a_p = 0.52560 (3)$ | 1.0086 | 0.14645 (2) |
| | 923 | 0.520 | 0.240 | Tetragonal | $t'$ | $a_p = 0.52578 (2)$ | 1.0092 | 0.14669 (1) |
| | 873 | 0.443 | 0.279 | Tetragonal | $t'$ | $a_p = 0.52585 (4)$ | 1.0093 | 0.14676 (3) |
| Starting sample | 0 | | Tetragonal | $t'$ | $a_p = 0.52588 (3)$ | 1.0093 | 0.14678 (2) |
| Omata et al. [8] 1123 | 0.774 | 0.113 | Tetragonal | $t'$ | $a_p = 0.52571 (3)$ | 1.0082 | 0.14649 (2) |
| 973 | 0.580 | 0.210 | Tetragonal | $t'$ | $a_p = 0.52583 (2)$ | 1.0088 | 0.14667 (1) |
| 873 | 0.406 | 0.297 | Tetragonal | $t'$ | $a_p = 0.52598 (3)$ | 1.0091 | 0.14684 (2) |
| Starting sample | 0 | | Tetragonal | $t'$ | $a_p = 0.52605 (2)$ | 1.0091 | 0.14689 (1) |

$^a$ The number in the parenthesis shows the standard deviation estimated in the last digit.

$^b$ The lattice parameters for the tetragonal phases of $t'$ and $t'_\text{meta}$ were adopted assuming a pseudo-fluorite unit cell. Actual lattice parameters $a_0$ and $c_0$ of the dimolecular unit cell based on the space group of P4$_2$/nmc were expressed by $a_0 = a_p\sqrt{2}$ and $c_0 = c_p$, respectively.

apparent intensity ratio of the peaks around 530 and 560 cm$^{-1}$, $I_{530}/I_{560}$, decreased. As the intensity of the peak around 560 cm$^{-1}$ was increased, the peak around 636 cm$^{-1}$ appeared to move toward a lower wave number. For the tetragonal phase obtained from $\delta = 0.145$ ($y = 0.710$) at $T_{\text{red}} = 1073$ K, the peak around 530 cm$^{-1}$ could not be isolated; further, a peak around 132 cm$^{-1}$ split into two bands at 138 and 115 cm$^{-1}$. These distinctive features were in excellent agreement with those of $t'_\text{meta}$(Ce0.5Zr0.5)O2 reported previously [8].

3.3. EGA results

Fig. 6 shows EGA results for the metastable tetragonal (Ce0.5Zr0.5)O2 prepared from the precursors, which were obtained in the heating-reduction runs shown in Fig. 3. The previous result for the cubic $\kappa$ phase is indicated by a dashed line for a comparison [3]. The J$_0$−$T$−$t$ curves for the $t'$ and reoxidized phase obtained from $\delta = 0.379$ ($y = 0.242$) at $T_{\text{red}} = 773$ K were almost overlapped. As the $\delta$ value decreased, the peak on the J$_0$−$T$−$t$ curve shifted toward a lower temperature. The peak on the J$_0$−$T$−$t$ curve for the $t'_\text{meta}$ obtained from $\delta = 0.111$ ($y = 0.778$) at $T_{\text{red}} = 1073$ K was still located at a higher temperature than that for the $\kappa$ phase. For the both cases, the oxygen release was started at low temperatures as 523 K.

The phases reoxidized at 873 K after the EGA was the pyrochlore-related type $\kappa$ phase. For instance, the XRD

Fig. 5. Raman spectra for $t'_\text{meta}$(Ce0.5Zr0.5)O2 prepared from the CeZrO3−δ precursor with various $\delta$ values, compared with that for starting $t'$(Ce0.5Zr0.5)O2.
Fig. 6.  $J_0 - T - t$ curves obtained for EGA analysis of $t'_\text{meta}$(Ce$_{0.5}$Zr$_{0.5}$)O$_2$ powders prepared from the Ce$_2$Zr$_2$O$_7$ precursor with various $\delta$ values, compared with those for starting $t'$(Ce$_{0.5}$Zr$_{0.5}$)O$_2$ and $\kappa$-CeZrO$_3$ [3].

Fig. 7. Powder X-ray diffraction patterns for the $\kappa$-CeZrO$_3$ phase reoxidized at 873 K after EGA.

pattern for the reoxidized sample with history of $\delta = 0.111$ at $T_{\text{red.}} = 1073$ K is shown in Fig. 7. Broad diffractions with indices of (111), (331), (333), and (531) were clearly observed; however, other superlattice diffractions characterizing the typical $\kappa$ phase obtained at $T_{\text{red.}} = 1573$ K [8,9] could not be observed. It was reported for the $\kappa$ phase obtained at $T_{\text{red.}} = 1323$ K that diffractions with indices of (111), (331), (333), and (531) were broadened due to anti-phase domain boundaries [8,9,18,19]. The present data on the appearance of the $t'_\text{meta}$ and $\kappa$ phases are in excellent agreement with the previous reports [8,9].

4. Discussions

First, the results on the XRD analysis and Raman spectroscopy are discussed. As seen in Fig. 4, the XRD patterns of the $t'_\text{meta}$ phases were almost identical to the $t'$ phase. This means that the $t'_\text{meta}$ phase has approximately the same structure as that of the $t'$ phase; it belongs to the space group of $P4_{1}2_{1}2_{1}$ and the atomic coordinates of cations and oxygen are (0,0,0) of the 2e site and (0, 0.5, $z$) with $z < 0.25$ of the 4d site, respectively [17]. In the previous paper [8], three of the authors (T.O., H.K., S.O.-Y.-M.) reported that, besides the Raman spectra, the parameters of $c_d/a_t$ ratio and unit cell volume for the tetragonal phases give the important information for distinguishing the $t'$ and $t'_\text{meta}$ phases; the values of the factors became small as the phases changed from $t'$ to the typical $t'_\text{meta}$. As seen in Table 1, for the precursor with $\delta = 0.371$ ($y = 0.258$) at $T_{\text{red.}} = 773$ K, the $c_d/a_t$ ratio and unit cell volume of the reoxidized tetragonal phase agreed with those of the $t'$; further, any difference could not be observed in the Raman spectra. The tetragonal phase obtained by the reoxidation was $t'$ phase. When the reducing ratio; $y$ became large as 0.443, i.e. $\delta = 0.279$, the unit volume of the reoxidized tetragonal phase was slightly decreased; the peak around 636 cm$^{-1}$ observed in the Raman spectrum for the $t'$ shifted slightly toward a lower wave number. In the previous work, the feature of the $t'_\text{meta}$ did not appear for $y = 0.406$ ($\delta = 0.297$). Thus, the border determining the appearance of a metastable tetragonal $t'_\text{meta}$ phase may exist around the reducing ratio; $y = 0.42$ and $\delta = 0.29$.

The $J_0$-$T$-$t$ curve obtained by the EGA analysis for the sample prepared from the precursor with $\delta = 0.379$ at $T_{\text{red.}} = 773$ K nearly coincided with that for $t'$; two peaks on the curve could be observed, which was a distinct feature for $t'$ phase. The EGA results were consistent completely with those of the XRD and Raman spectra. When the reducing ratio was 595, i.e. $\delta = 0.203$, the peak on the $J_0$-$T$-$t$ shifted slightly but clearly toward a lower temperature, and its shape differed from that for the $t'$ phase. When the reducing ratio was large as 0.778, i.e. $\delta = 0.111$, the peak temperature appearing on the $J_0$-$T$-$t$ curve was decreased further. Generally, the kinetic properties, e.g. oxygen diffusion in the sample, together with its thermodynamic properties, may be considered as a factor determining the oxygen release rate from the sample. However, we have proved in many reports [3,6,7,16] that the oxygen release behavior of $x$CeO$_2$-$\left(1-x\right)$ZrO$_2$ powders reflects strongly
the thermodynamic behavior of the respective phase. The typical result has been obtained for the \( \kappa \) phase being more unstable than the \( t' \) phase. The thermodynamic instability of the \( \kappa \) phase has been confirmed by emf measurements using an electrochemical cell [20]. For EGA analysis, the \( \kappa \) phase released oxygen rapidly at low temperatures as 673 K, as indicated by a dashed line in Fig. 6. The swift oxygen diffusion is the reason why the \( x\text{CeO}_2-(1-x)\text{ZrO}_2 \) powders have been used as the promoter for automotive exhaust gases oxidizing harmful CO and hydrocarbons to CO\(_2\) and H\(_2\)O gases [21–23]. Moreover, the oxygen analyzer with significantly high sensitivity has been used in the present study; smaller amounts of samples leads to much isolated particles situation [11,14].

According to the EGA results, the \( t'_{\text{meta}} \) phase appeared to be thermodynamically less stable than the \( t' \) phase. This results is consistent with the phenomena reported previously that the \( t'_{\text{meta}} \) phase became the \( t' \) phase above 1273 K, as heating it in O\(_2\) gas [10]. As the reducing ratio was increased, i.e. the \( \delta \) value of the precursor was decreased, the metastable \( t'_{\text{meta}} \) phase obtained more unstable. The thermodynamic behavior of \( t'_{\text{meta}} \) phases is not uniform but appears to change rather continuously with the \( \delta \) value.

Second, we discuss the structure of the \( t'_{\text{meta}} \) phase. According to the XRD analysis, the \( c_{\text{f/d}}/a_{\text{c}} \) value and unit cell volume of \( t'_{\text{meta}}-(\text{Ce}_0.5\text{Zr}_0.5)\text{O}_2 \) phase appeared to change continuously with the \( \delta \) value of the precursor. In the previous report [8], it was revealed that the oxygen parameter, \( z \), can be excellently related to the \( c_{\text{f/d}}/a_{\text{c}} \) ratio assuming a pseudofluorite unit cell for tetragonal phases with various \( \text{ZrO}_2 \)-based compositions. Based on the relationship, the oxygen parameters were estimated to be 0.218 and 0.220 for the starting \( t'-(\text{Ce}_0.5\text{Zr}_0.5)\text{O}_2 \) and \( t'_{\text{meta}}-(\text{Ce}_0.5\text{Zr}_0.5)\text{O}_2 \) from \( \delta = 0.113 \) at \( T_{\text{red}} = 1123 \) K, respectively. It may be inferred that the oxygen parameter, \( z \), changes continuously between \( t'_{\text{meta}} \) and \( t' \) phases, although the difference in \( z \) is very small. Furthermore, we have inferred that an essential effect altering the thermodynamic behavior of the \( t'_{\text{meta}} \) may exist, except for change in the oxygen parameter [7]. As the reduction ratio is increased, the Ce and Zr ions in the precursor begin to be ordered, respectively, in the (110) direction. Finally, the intercalation of oxygen produces the \( \kappa \) phase keeping the ordered arrangement of Ce and Zr ions. As clear from the XRD patterns, however, the Ce and Zr ions in both the \( t'_{\text{meta}} \) and \( t' \) phases are disordered. We have to introduce a new idea concerning the disordered arrangement. The \( t'-(\text{Ce}_0.5\text{Zr}_0.5)\text{O}_2 \) phase prepared from the precursor of the CaF\(_2\)-type cubic phase at high temperatures as 1923 K must possess almost strict random distribution of Ce and Zr ions. If we could detect the Ce/Zr mole ratio in various microscopic regions of the \( t'-(\text{Ce}_0.5\text{Zr}_0.5)\text{O}_2 \) phase, e.g. in nanometer scale or infinitesimal scale, the Ce/Zr molar ratio must be larger or smaller than unity; the strict random distribution means this situation. Alternately, we can imagine another situation that the Ce/Zr mole ratio in any microscopic region approaches unity continuously; the \( t'_{\text{meta}} \) may correspond to the latter case. The structural difference between the \( t'_{\text{meta}} \) and \( t' \) phases possibly lies in the distribution of the Ce and Zr ions in the microscopic region, although the both phases possess the disordered arrangement of the Ce and Zr ions. Fig. 8 shows an illustration of the qualitative relation between the degree of random on the cation sites and the thermodynamic stability of the \( t' \), \( t'_{\text{meta}} \) and \( \kappa \) phases with CeZrO\(_2\) composition; the \( t'_{\text{meta}} \) phases with various Gibbs energies are depicted. Vacancies may exist on the cation sites, together with the Ce and Zr ions.

When the \( \kappa \) phases was annealed in O\(_2\) gas at high temperatures as 1423 K, the very stable tetragonal \( t' \) phase appeared [3]. The \( t' \) phase is not shown in this figure, because its structural feature is not still clear. If the Ce/Zr mole ratio in any microscopic region of the \( t'_{\text{meta}} \) approaches unity continuously, the entropy value of the \( t'_{\text{meta}} \) becomes smaller than the \( t' \) and therefore, its thermodynamic stability should be decreased. Furthermore, the thermodynamic properties of the \( t'_{\text{meta}} \) and \( t' \) may vary continuously between them. To confirm this deduction, investigations in microscopic scale, e.g. using EXAFS are needed.

### 5. Conclusions

Tetragonal CaF\(_2\)-related-type \( t'-(\text{Ce}_0.5\text{Zr}_0.5)\text{O}_2 \) phase was reduced at 773 K \( \leq T_{\text{red}} \leq 1073 \) K to prepare precursors with various oxygen compositions: CeZrO\(_{3.5+\delta}\). Metastable tetragonal \( t'_{\text{meta}}-(\text{Ce}_0.5\text{Zr}_0.5)\text{O}_2 \) phases were prepared by oxidizing in O\(_2\) at 873 K the precursors. The tetragonal phases obtained were subjected to the XRD and Raman spectroscopic analyses, and EGA analysis by heating the samples at a constant rate. The results obtained are summarized as follows:

(i) For the precursor with \( \delta = 0.379 \) prepared at \( T_{\text{red}} = 773 \) K, the oxygen release behavior of the reoxidized...
tetragonal phase agreed with that of the \( t' \). The reoxidized phase was the \( t' \) phase.

(ii) For the precursors with \( \delta = 0.203 \) and 0.111 prepared, respectively, at \( T_{\text{red}} = 923 \) and 1073 K, the temperatures exhibiting the maximum release rate of oxygen from the \( t'_{\text{meta}} \) was lower than that from the \( t' \) phase; the temperature appeared to be decreased with decreasing the \( \delta \) value.

(iii) For \( \delta = 0.279 \), small but clear features of the \( t'_{\text{meta}}-(CeO\text{g}_{0.5}Zr\text{g}_{0.5})\text{O}_2 \) appeared in the XRD data and Raman spectrum. With decreasing the \( \delta \) value, the data approached to those for the typical \( t'_{\text{meta}} \) the border for the appearance of the \( t'_{\text{meta}}-(CeO\text{g}_{0.5}Zr\text{g}_{0.5})\text{O}_2 \) was inferred to be around \( \delta = 0.29 \).

(iv) It was experimentally demonstrated that the thermodynamic stability of the \( t'_{\text{meta}}-(CeO\text{g}_{0.5}Zr\text{g}_{0.5})\text{O}_2 \) is lower than that of the \( t' \); further, the \( t'_{\text{meta}} \) phase formed from a smaller \( \delta \) value became more unstable.

(v) For the \( t' \) and \( t'_{\text{meta}} \) phases exhibiting various thermodynamic behaviors, difference in the random degree of the Ce and Zr ions on the cation sites was suggested, in spite of the disordered arrangement of the Ce and Zr ions in them. The Ce/Zr molar ratio in any microscopic region of the \( t'_{\text{meta}}-(CeO\text{g}_{0.5}Zr\text{g}_{0.5})\text{O}_2 \) is possibly closer to unity than that in the \( t'-(CeO\text{g}_{0.5}Zr\text{g}_{0.5})\text{O}_2 \).

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