Valence Change of Cations in Ceria-Zirconia Solid Solution Associated with Redox Reactions Studied with Electron Energy-Loss Spectroscopy

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It has been known that the ceria-zirconia solid solutions ($Ce_2Zr_2O_{7+x}$, $0 \leqq x \leqq 1$) have an excellent ability for oxygen absorption/release. The local charge states of cations in the CeO_2-ZrO_2 solid solutions have been studied by means of electron energy-loss spectroscopy (EELS) attached to a transmission electron microscope. The relative intensity of cerium-$M_{4,5}$ white-line peaks from $Ce_2Zr_2O_7$, $Ce_2Zr_2O_{7.5}$ and $Ce_2Zr_2O_8$ showed a systematic change, which corresponded to the valence change of cerium; Ce^{3+} in $Ce_2Zr_2O_7$, Ce^{4+} in $Ce_2Zr_2O_8$. By contrast, the valence of the zirconium ions, which are mainly at the nearest neighbor sites of absorbed or emitted oxygen atoms, remains to be quaternary irrespective of oxygen contents. It was found that the energy-loss near edge structure (ELNES) of the cerium-$M_{4,5}$ edge in $Ce_2Zr_2O_{7.5}$ was well reproduced by the sum of the ELNES profiles of $Ce_2Zr_2O_7$ and $Ce_2Zr_2O_8$ with an equal weight, the phenomenon of which is known as the 'valence fluctuation,' or 'mixed valence state,' often observed in rare earth metal compounds.

1. Introduction

CeO_2-based three-way catalysts (TWCs) have attracted much attention as a candidate element for controlling the air pollution from automotive emissions. Recently, it was found that the oxygen absorption/release capacity of CeO_2 was significantly improved by addition of ZrO_2.[1–3] A ceria-zirconia solid solution ($Ce_2Zr_2O_7$) having the pyrochlore structure, which is prepared by reduction treatment of the 1:1 mixture of CeO_2 and ZrO_2 powders at a high temperature, is now widely used as TWCs in automobiles because the reduced solid solution with an equimolar composition of CeO_2 and ZrO_2 possesses a particularly excellent ability for oxygen absorption/release.[4–6] $Ce_2Zr_2O_7$ is fully oxidized to $Ce_2Zr_2O_8$, in which oxygen atoms are absorbed/released into/from particular atomic sites, depending on the degree of oxidation/reduction. However, it is not yet fully clear why the oxygen absorption/release ability is improved by addition of ZrO_2.

$Ce_2Zr_2O_7$ has the pyrochlore structure with a cubic symmetry, the building blocks of which are cerium coordinated by eight oxygen atoms and zirconium by six oxygen atoms, and the two cations construct a NaCl-type ordered structure. From this feature the structure intrinsically possesses ordered oxygen vacancies at the nearest neighbor sites of zirconium[7] and hence $Ce_2Zr_2O_7$ can store oxygen to fill the oxygen vacancies up to the composition of $Ce_2Zr_2O_8$. It is considered that this particular property enables this material the reversible reactions of $Ce_2Zr_2O_7 + 1/2O_2 \Leftrightarrow Ce_2Zr_2O_8$, release of oxygen under a low oxygen pressure and absorption of oxygen under a high oxygen pressure at a high

temperature.[4–6]

Sasaki *et al.* observed the crystal structure change associated with the oxygen absorption/release in the ceria-zirconia solid solution, using X-ray diffraction, electron diffraction and high-resolution transmission electron microscopy: They found that $Ce_2Zr_2O_7$, the starting material, absorbed oxygen even at room temperature, when exposed to air for a long term, to form the metastable intermediate phase of $Ce_2Zr_2O_{7.5}$. The absorbed oxygen selectively occupied the oxygen vacancy sites, which changed the space group from $Fd\bar{3}m$ to $F\bar{4}3m$.[8,9]

The local charge compensation of $Ce_2Zr_2O_{7+x}$ ($0 \leqq x \leqq 1$) associated with the oxygen absorption/release is usually accommodated with the local symmetry change around the cation atoms or the valence change of the cation atoms themselves. Actually both effects have been already suggested in this material,[7,10] and the valence change of cerium ion from 4 to 3 was observed during the reduction of CeO_2 and $Ce_2Zr_2O_8$.[7] The valence change should proceed so as to satisfy the electrical neutrality condition according to the chemical composition change, which has not yet been clearly confirmed. Roughly speaking, oxygen atoms occupy three types of octahedral sites of the cation lattice, one surrounded by four cerium ions, another by four zirconium ions and the other by two cerium and two zirconium ions. Curiously, the oxygen site related to the oxygen absorption/release is the one surrounded by four zirconium ions rather than the one surrounded by cerium ions.[11] Therefore, the oxygen absorption/release characteristic is determined by a peculiar electric charge balance in this crystal structure, and this feature can be a key to solve why the oxygen absorption/release characteristic in this material is excellent. Diffraction studies for crystallographic structure analysis have been mainly conducted on this material, while there have been few

reports available on the local electric charge distributions.

From the above viewpoint, we applied electron energy-loss spectroscopy (EELS) in order to examine the change of local electric charge distributions associated with the oxygen absorption/release in $Ce_2Zr_2O_{7+x}$.

2. Experimental

The samples used for the present experiments were prepared by the following procedures: first the precursor in which CeO_2 and ZrO_2 1:1 mol% were co-precipitated in the aqueous nitrate solution was synthesized. The precursor was heated in the reducing furnace under the argon gas atmosphere up to 1700 K, which changed the precursor to $Ce_2Zr_2O_7$ having the pyrochlore structure.[4–6] The product was then crushed into powder in the mortar. The $Ce_2Zr_2O_7$ sample powder was preserved in acetone for antioxidation, for it can absorb oxygen from the ambient atmosphere at room temperature. The $Ce_2Zr_2O_7$ powder was heat-treated under the oxygen atmosphere at 1100 K to obtain the $Ce_2Zr_2O_8$ oxide. The intermediate phase, $Ce_2Zr_2O_{7.5}$, was prepared just by exposing the $Ce_2Zr_2O_7$ powder to air for nearly 1 year.[8] The $Ce_2Zr_2O_8$ and $Ce_2Zr_2O_{7.5}$ samples did not seem to change to another phase by their exposure to air at room temperature.

The samples were put on carbon microgrid films and then immediately inserted into the microscope vacuum to avoid any further oxidation or reduction. The observation was performed with an 300 kV electron microscope (Hitachi H-9000NAR) equipped with GATAN imaging filter, GIF, and a 200 kV electron microscope (JEOL JEM-2010F) equipped with a parallel electron energy-loss spectrometer.

3. Results

A representative EEL spectra taken from $Ce_2Zr_2O_8$ is shown in Fig. 1, where oxygen K-core loss peak at 532 eV, Cerium M_5 and M_4 edge spectra around 900 eV, and zirconium L_3 and L_2 edge spectrums at 2222 eV. In the present study, we focus on this cerium $M_{4,5}$ edge and zirconium $L_{2,3}$ edge spectra.

3.1 ELNES of cerium-$M_{4,5}$ edge

Figure 2 shows energy-loss near edge structure (ELNES) of $M_{4,5}$ edges of $Ce_2Zr_2O_7$, $Ce_2Zr_2O_{7.5}$ and $Ce_2Zr_2O_8$, in which the pre-edge and post-edge continuum background components were subtracted. The pre-edge background was modeled with a power law, AE^{-R} (E: energy loss, A, R: fitting parameters), in a conventional manner and the shape of the
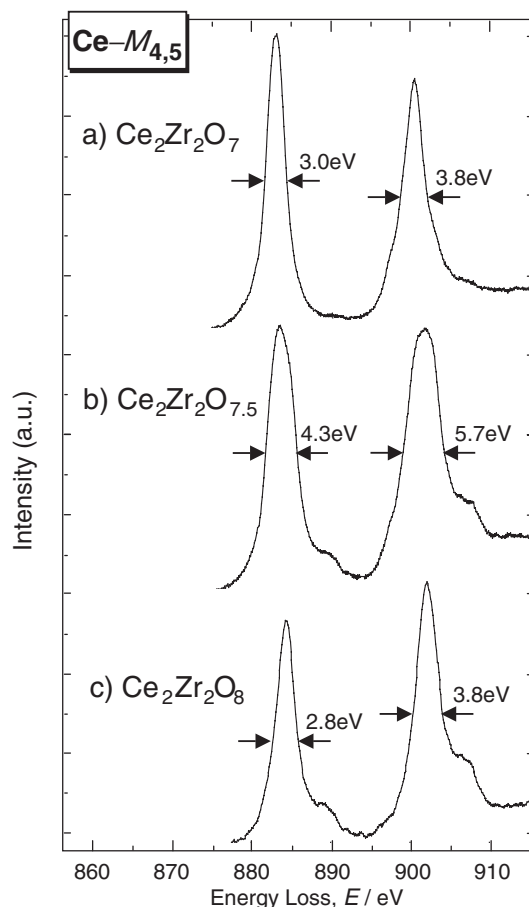
Fig. 2 Ce-$M_{4,5}$ white-line peaks obtained from (a) $Ce_2Zr_2O_7$, (b) $Ce_2Zr_2O_{7.5}$ and (c) $Ce_2Zr_2O_8$. FWHM of each peak is indicated. The relative white-line peak intensity, $I(M_4)/I(M_5)$, is 0.95, 1.10 and 1.25 for (a), (b) and (c), respectively.
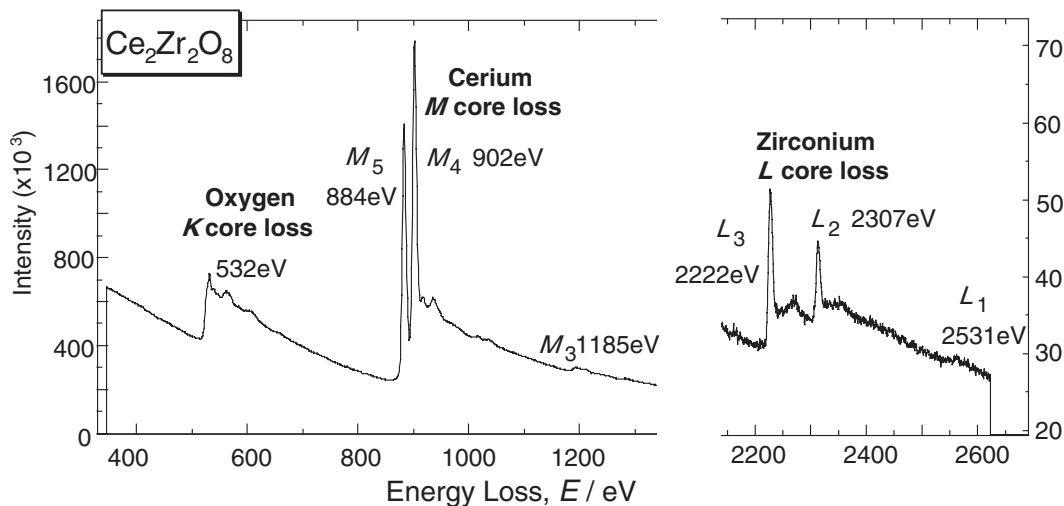
Fig. 1 O-K, Ce-M and Zr-L core-loss spectra obtained from $Ce_2Zr_2O_8$.

post-edge continuum was deduced from the Hartree-Slater calculations.[12] Two sharp peaks close to the ionization threshold are called 'white-line', characteristic to the $L_{2,3}$ edges of transition metals and the $M_{4,5}$ edges of rare earths. The energy separation of these peaks reflects the spin-orbit splitting of the $3d$ initial states in the transition and their relative intensity is expected to change with the occupancy of the $4f$ final state orbital. It was actually experimentally shown that the relative intensity of the white-line peaks of the $4f$ rare earth elements from La to Lu (lanthanides) is a monotonic function of final-state occupancy or atomic number.[12] The relative intensity of white-line peaks, $I(M_4)/I(M_5)$, is therefore a potential source of information about oxidation state.[13–15]

The value of $I(M_4)/I(M_5)$ for $Ce_2Zr_2O_7$ (Fig. 2(a)) and $Ce_2Zr_2O_8$ (Fig. 2(c)) was estimated to be 0.95 and 1.25, respectively. For comparison cerium $M_{4,5}$ edges from CeF_3 and CeO_2 are shown in Fig. 3, as reference spectra of Ce^{3+} and Ce^{4+}, respectively. The value of $I(M_4)/I(M_5)$ for CeF_3 was 0.95 and for CeO_2 1.25. It can be hence interpreted that the valence state of cerium changed from Ce^{3+} to Ce^{4+} by the oxidation from $Ce_2Zr_2O_7$ to $Ce_2Zr_2O_8$.

In the meantime, the value of $I(M_4)/I(M_5)$ for $Ce_2Zr_2O_{7.5}$ (Fig. 2(b)) was estimated to be 1.10, which coincides with the arithmetic mean of 0.95 and 1.25. This means that the apparent valence of cerium is 3.5. Such a phenomenon is called 'valence fluctuation' or 'mixed valence state', known as one of the characteristic behaviors of $4f$ rare earth metal compounds.[16]

3.2 ELNES of zirconium-$L_{2,3}$ spectrum

Figure 4 shows zirconium $L_{2,3}$ edge spectra of $Ce_2Zr_2O_7$, $Ce_2Zr_2O_{7.5}$ and $Ce_2Zr_2O_8$. And Fig. 5 shows a reference

Fig. 4   Zr-$L_{2,3}$ peaks obtained from (a) $Ce_2Zr_2O_7$, (b) $Ce_2Zr_2O_{7.5}$ and (c) $Ce_2Zr_2O_8$.

Fig. 5   Zr-$L_{2,3}$ peaks obtained from ZrO_2 (Zr^{4+}) reference sample.
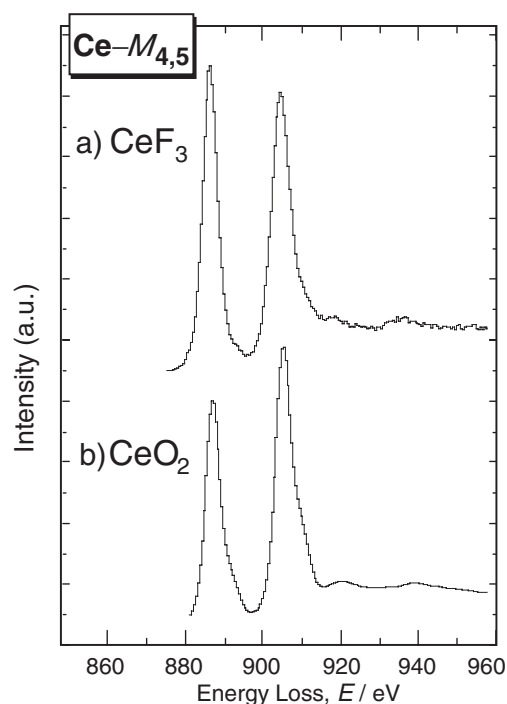

Fig. 3   Ce-$M_{4,5}$ white-line peaks obtained from (a) CeF_3 (Ce^{3+}) and (b) CeO_2 (Ce^{4+}) reference samples. The relative white-line peak intensity, $I(M_4)/I(M_5)$, is 0.95 and 1.25, respectively.
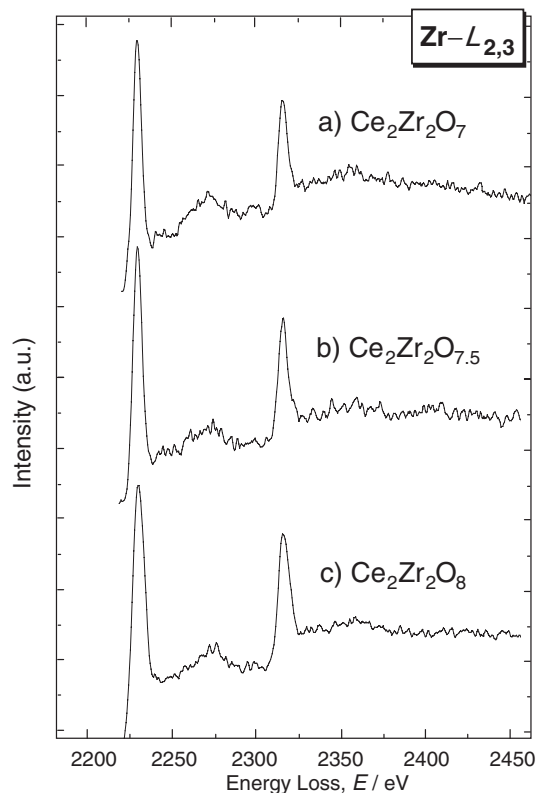
zirconium $L_{2,3}$ edge spectrum from ZrO_2. The series of the spectra indicates that the valence state of zirconium remained to be Zr^{4+} throughout the oxidation process.

4.   Discussion

4.1   Local charge equilibrium associated with oxygen absorption

In crystals having a large measure of ionic bond character, such as the present ceria-zirconia solid solutions, the structure is in large part determined on the basis of how positive and negative ions can be stacked together on a lattice to maximize electrostatic attractive forces and minimize electrostatic repulsion. An empirical but convenient rules,

derived by Pauling,[17] can give a guideline to achieve this minimum-energy condition based on properties of the ions used. In general cations are smaller in size than anions, and many ionic structures can be built up by putting small cations in the interstices between larger anions (coordination polyhedron). According to the Pauling's first rule,[17] the coordination number of anions around a cation is determined by the geometry necessary for the cation to remain in contact with each anion and the geometry is fixed by the radius ratio of the cation-anion combination. A particular coordination number is thus stable as long as the cation-anion radius ratio is larger than a certain critical value. In other words, a larger number of anions are necessary to stabilize the coordination polyhedron containing a cation having a larger ionic radius. When looking into the case of $Ce_2Zr_2O_7$, one can see that the Pauling's rule holds well: the ionic radius of Ce^{3+} and Zr^{4+} is 0.10 nm and 0.07 nm respectively,[18] and the larger Ce^{3+} ions are surrounded by eight oxygen atoms, while the smaller Zr^{4+} by six. It can be thus explained why oxygen vacancies are introduced at the nearest neighbor sites of Zr^{4+} in $Ce_2Zr_2O_7$.

On the other hand, the present EELS measurements showed that the valence of the zirconium ion remained unchanged, while the valence of the cerium ion successively changed from 3 to 3.5 and 4, with increasing the oxygen content (by filling the oxygen vacancies near the zirconium ions) in the transformations from $Ce_2Zr_2O_7$ to $Ce_2Zr_2O_{7.5}$ and $Ce_2Zr_2O_8$. It has been reported that the cubic symmetry is retained by this change in the oxygen content, and the interatomic distances between the cations and oxygen only slightly change by the transformation between $Ce_2Zr_2O_7$ and $Ce_2Zr_2O_{7.5}$, while the transformation between $Ce_2Zr_2O_{7.5}$ and $Ce_2Zr_2O_8$ accompanies considerable atomic shuffles in the oxygen positions.[8] These features can be again explained qualitatively in terms of the Pauling's rule: with increasing the oxygen content, the coordination number (the number of oxygen ions) of zirconium ions increases, while the total charge neutrality is compensated by the valence change of cerium ions. It is considered that the cation-anion radius ratio of zirconium is still smaller than the critical value required for stabilizing the coordination polyhedra in the $Ce_2Zr_2O_{7.5}$ intermediate phase, whereas a larger coordination number of zirconium in $Ce_2Zr_2O_8$ can no longer accommodate the radius ratio and requires the distortion of coordination polyhedra.

4.2 Valence fluctuation at intermediate phase $Ce_2Zr_2O_{7.5}$

As described in 3.1, cerium ions in the $Ce_2Zr_2O_{7.5}$ intermediate phase demonstrates a 'mixed valence state' of $Ce^{3.5+}$. It should be noted here that the present phenomenon does not result from two kinds of cerium sites, each occupied by Ce^{3+} and Ce^{4+} separately, because the cerium site is crystallographically all equivalent in the $Ce_2Zr_2O_{7.5}$ structure.[7]

The valence fluctuation or mixed valence state can be thought of as a mixture of $4f^n$ and $4f^{n-1}$ ions, the energies of which are nearly degenerate. $4f$ charge fluctuations between the two configurations occur on a time scale τ_{vf}, so-called valence fluctuation time. Therefore, experiments which
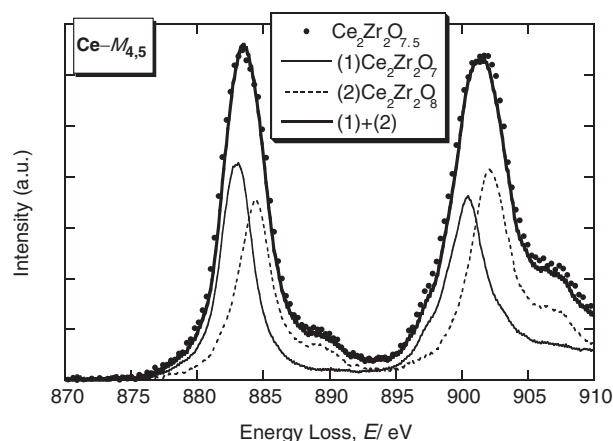

Fig. 6　Nomogram showing that experimental Ce-$M_{4,5}$ edge (solid circles) in $Ce_2Zr_2O_{7.5}$ is well reproduced by the sum (thick solid line) of Ce-$M_{4,5}$ edges in $Ce_2Zr_2O_7$ (thin solid line) and $Ce_2Zr_2O_8$ (broken line).

probe the sample on a time scale much shorter than τ_{vf} will see both configurations, while experiments which probe on a time scale longer than τ_{vf} will see only one intermediate configuration. EELS in general should be classified into the former category. The cerium $M_{4,5}$ spectrum of the $Ce_2Zr_2O_{7.5}$ intermediate phase should hence exhibit a profile as if a cerium ion may take both Ce^{3+} and Ce^{4+} configurations with an equal probability, since the apparent valence was deduced to be 3.5, as shown in sec. 3.2. As a matter of fact, Ce-$M_{4,5}$ ELNES of $Ce_2Zr_2O_{7.5}$ was perfectly reproduced by the sum of the two other spectra from $Ce_2Zr_2O_7$ and $Ce_2Zr_2O_8$ with an equal weight, as shown in Fig. 6. The apparent increase in the FWHM of the white-line in $Ce_2Zr_2O_{7.5}$ thus originates from the different spin-orbit splitting widths of Ce^{3+} and Ce^{4+} configurations.

5.　Summary

Changes in the valence state of cerium associated with oxygen absorption of $Ce_2Zr_2O_{7+x}$ ($0 \leqq x \leqq 1$) were studied by means of electron energy-loss spectroscopy (EELS). The results obtained are summarized in the following:

(1) The apparent valence state of cerium ion was Ce^{3+}, $Ce^{3.5+}$ and Ce^{4+} for $Ce_2Zr_2O_7$, $Ce_2Zr_2O_{7.5}$ and $Ce_2Zr_2O_8$ respectively. On the other hand, the valence state of zirconium ion remained Zr^{4+} for any case among the three although oxygen atoms filled the structural vacancies located at the nearest neighbor sites of zirconium.

(2) The total charge neutrality associated with the oxygen absorption/release is compensated by the valence change of the cerium ion. And it was found that the Pauling's rules could give a qualitative explanation on the reported structural changes in the transformations from $Ce_2Zr_2O_7$ to $Ce_2Zr_2O_{7.5}$ and $Ce_2Zr_2O_8$.

(3) A 'mixed valence state' of cerium ion in the $Ce_2Zr_2O_{7.5}$ intermediate phase was found and its Ce-$M_{4,5}$ edge profile can be perfectly reproduced by the sum of the two Ce-$M_{4,5}$ edge profiles from $Ce_2Zr_2O_7$ and $Ce_2Zr_2O_8$ phases. This indicates that the electronic configuration of each cerium ion fluctuates between Ce^{3+} and Ce^{4+} configurations.

We believe that the present results above can be a

milestone for understanding why the ceria-zirconia solid solution exhibits the excellent oxygen absorption/release properties.

Acknowledgements

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