

Electronic Structure of $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-\delta}$ Probed by Soft-X-Ray Spectroscopy

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The electronic structure of Nd^{3+} -doped CeO_2 ($\text{Ce}_{1-x}\text{Nd}_x\text{O}_2$) was studied by X-ray absorption spectroscopy (XAS) and resonant photoemission spectroscopy (RPES). The XAS spectra show that the intensity of the conduction band, which is mainly composed of the O 2*p* state hybridized with the unoccupied Ce 4*f* state, decreases with increasing Nd^{3+} concentration. The RPES spectra show that the Ce 4*f* partial density of states in the valence band decreases with increasing Nd^{3+} concentration. These findings indicate that the hybridization effect between the Ce 4*f* and O 2*p* states decreases with increasing Nd^{3+} concentration. [DOI: 10.1143/JJAP.43.L1463]

KEYWORDS: Nd^{3+} -doped CeO_2 ($\text{Ce}_{1-x}\text{Nd}_x\text{O}_2$), resonant photoemission spectroscopy (RPES), electronic structure, hybridization effect, effective charge

Solid oxide fuel cell in intermediate temperature region, which operates at less than 800°C, has attracted the attention. The decrease in operating temperature leads to the cost reduction and higher durability of the system. Most attention has been focused on fluorite-type oxide CeO_2 . In particular, rare-earth-doped CeO_2 is a promising material for both an electrolyte and an anode for solid oxide fuel cell because of its high oxygen conductivity at lower temperature and electron-oxygen ion mixed conduction in reducing atmospheres.^{1–3)} The performance of the solid state material is greatly related to mass transport properties in the bulk and at the surface.

In recent years, the structural and transport properties of doped CeO_2 , such as $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-\delta}$, $\text{Ce}_{1-x}\text{Yb}_x\text{O}_{2-\delta}$ and $\text{Ce}_{1-x}\text{Gd}_x\text{O}_{2-\delta}$, have been extensively investigated by Mizusaki groups.^{4–10)} The hydrogen solubility in doped CeO_2 is higher than that of undoped CeO_2 .¹⁰⁾ They studied the mass transport properties of $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}$ at the surface and in the bulk.^{8,9)} The surface reaction rate constants (*k*) are not directly related with oxygen partial pressure but depend on the gas species and the composition. The isotope exchange depth profiling with secondary ion mass spectrometry (SIMS) was done to examine the relationship between *k* and surface exchange coefficients.⁸⁾ They proposed that electrons, which result from reduction of Ce ions from Ce^{4+} to Ce^{3+} , cause the electronic conductivity. However, this fact has not been directly confirmed by spectroscopic methods, such as photoemission spectroscopy (PES) and X-ray absorption spectroscopy (XAS).

In this work, the electronic structure in the surface state of Nd^{3+} -doped CeO_2 ($\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-\delta}$) were studied by resonant-PES (RPES) and XAS. The PES is surface sensitive because the mean free path of an electron is very short compared with that of light. As reference, the XAS spectra were also measured in order to confirm the Nd^{3+} substitution for Ce^{4+} site. It has been reported that the electrical and transport properties of $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-\delta}$ is similar to those of $\text{Ce}_{1-x}\text{Yb}_x\text{O}_{2-\delta}$ and $\text{Ce}_{1-x}\text{Gd}_x\text{O}_{2-\delta}$.^{1,11)} Thus, we believe that the result of electronic structure obtained in this study give new information for doped CeO_2 .

$\text{Ce}_{1-x}\text{Nd}_x\text{O}_2$ samples were sintered ceramics prepared by

the solid-state reaction of Nd_2O_3 and CeO_2 at 1573 K, and pressed into cylinders of $\phi 13\text{ mm} \times 8\text{ mm}$, then sintered again in air at 1923 K for 15 h. The Nd^{3+} concentrations were $x = 0, 0.10$ and 0.20 . The samples were confirmed as having a single phase with a fluorite structure by the powder X-ray diffraction analysis. The detailed electrical and structural properties will be published elsewhere.¹¹⁾

RPES and XAS measurements were carried out at the Photon Factory of the High Energy Accelerator Organization, Tsukuba in Japan. Synchrotron radiation was monochromatized using a varied-line spacing plane grating whose average groove density is 1000 lines/mm. The PES spectra were measured by an electrostatic hemispherical analyzer whose radius is 100 mm. The XAS spectra were measured using a Si photodiode. The samples were scraped *in situ* with a diamond file in a vacuum of 4.0×10^{-10} Torr in order to obtain a clean surface. The total energy resolutions of PES and XAS were approximately 40 meV and 100 meV, respectively. The energy axis was calibrated by measuring the 4*f* core level of Au film.

Figure 1 shows the O 1*s* XAS spectra as a function of Nd^{3+} concentration in $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-\delta}$. The O 1*s* XAS spectra were normalized by the Ce 5*d* peak of the conduction band, although its peak is not shown in this figure. From the dipole selection rule, it is understood that the O 1*s* XAS spectra of Ce oxides correspond to transitions from O 1*s* to the O 2*p* character.^{12,13)} The large band around 531 eV is mainly composed of the O 2*p* state hybridized with the unoccupied Ce 4*f* state. The intensity of large band around 531 eV decreases with increasing Nd^{3+} concentration, indicating that Nd^{3+} are substituted into the Ce^{4+} site in CeO_2 . On the other hand, the intensity of peak δ at the bottom of the Ce 4*f* conduction band increases with increasing Nd^{3+} concentration. Similar peak has been observed in Y^{3+} -doped BaCeO_3 , which has the same electronic configuration with CeO_2 . The peak δ is considered to be the Ce 4*f*- or Nd 4*f* defect-induced level, although the origin is not clarified in this study.

Figure 2 shows the constant final state (CFS) spectrum of $\text{Ce}_{0.90}\text{Nd}_{0.10}\text{O}_2$ obtained by collecting photoelectrons with a kinetic energy of 19 eV. This spectrum is regarded as the

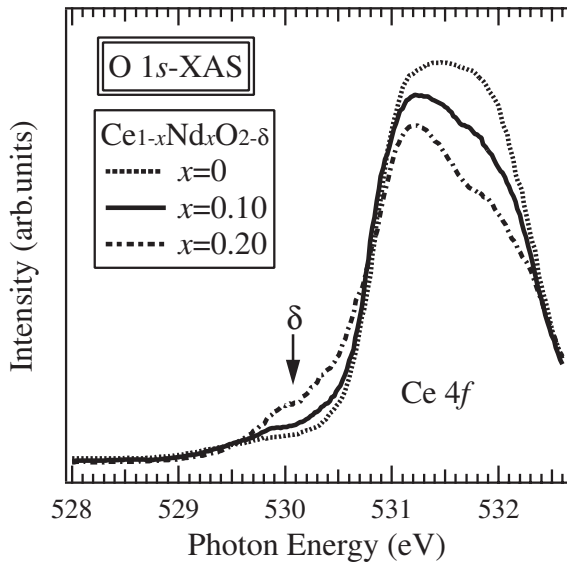


Fig. 1. O 1s XAS spectra as a function of Nd^{3+} concentration in $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-\delta}$.

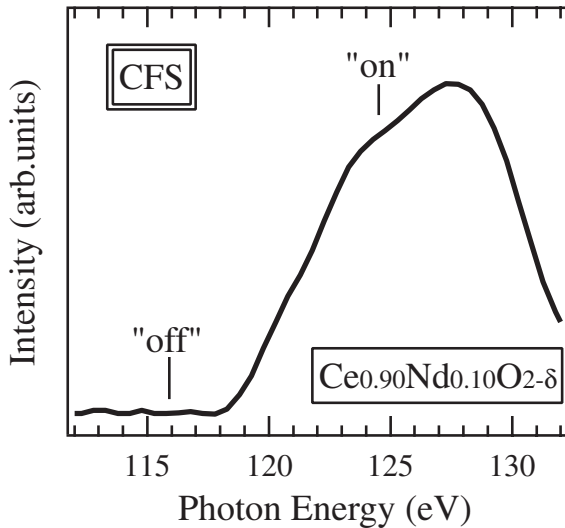


Fig. 2. CFS spectrum of $\text{Ce}_{0.90}\text{Nd}_{0.10}\text{O}_{2-\delta}$, corresponding to the $\text{Ce } 4d \rightarrow 4f$ giant absorption spectrum.

approximate absorption spectrum of $\text{Ce } 4d \rightarrow 4f$. The line shape and peak position of the CFS spectrum are similar to the $4d$ photoabsorption spectra of CeO_2 and BaCeO_3 .¹³⁻¹⁵ In the case of CeF_3 with electronic configuration of $4f^1$ (Ce^{3+}), the peak position shifts to the lower energy side than CeO_2 and BaCeO_3 .¹⁵ Thus, this result indicates that the electronic configuration of Ce in $\text{Ce}_{0.90}\text{Nd}_{0.10}\text{O}_2$ is mainly composed of $4f^0$ (Ce^{4+}). The vertical bars, which are labeled as "on" and "off", indicate the selected excitation energies for the RPES measurements.

Figure 3(a) shows the RPES spectra of $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-\delta}$ in the $\text{Ce } 4d \rightarrow 4f$ energy region. The off-resonance spectra, which reflect the total DOS of $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-\delta}$, have two peaks A and B. In the on-resonance spectra, the intensities of peaks A and B are enhanced by the $\text{Ce } 4d \rightarrow 4f$ excitation. The intensities of A and B peaks decrease with increasing Nd^{3+} concentration. The resonance effect of the peak B is stronger than that of the peak A.

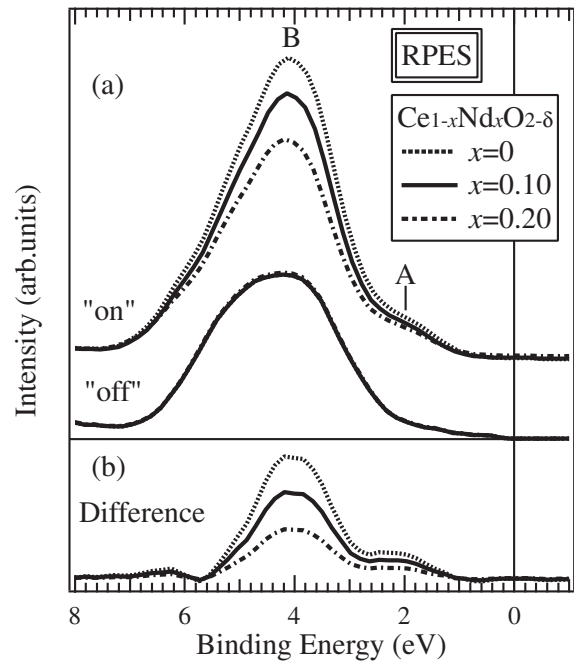


Fig. 3. (a) On- and off-resonance spectra as a function of Nd^{3+} concentration in $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-\delta}$. The on- and off-resonance spectra were measured at $h\nu = 124.5$ eV and 116.0 eV, respectively. (b) Difference spectra as a function of Nd^{3+} concentration in $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-\delta}$ obtained by subtracting the off-resonance spectra from the on-resonance spectra.

Figure 3(b) shows the difference spectra by subtracting the off-resonance spectra from the on-resonance spectra. The difference spectra correspond to the Ce $4f$ partial density of state (PDOS) in the valence band. The Ce $4f$ contribution is more significant in the higher binding energy (peak B), where the O $2p$ states have a larger admixture of Ce $4f$ states. In other words, the valence states originating from the O $2p$ states are hybridized with the Ce $4f$ states. Comparing the difference spectra, the Ce $4f$ PDOS decreases with increasing Nd^{3+} concentration. This result implies that the hybridization effect between the Ce $4f$ state and O $2p$ state decreases with increasing Nd^{3+} concentration. Such a hybridization effect has been reported in perovskite-type oxide BaTiO_3 ,¹⁶ which undergoes a ferroelectric phase transition at ~ 393 K. The valence band consists of O $2p$ state hybridized with Ti $3d$ state. The Ti-O hybridization effect in the paraelectric phase is stronger than that in ferroelectric phase. This originates the change of the bond length between Ti and O ions in BaTiO_3 . Similar situation is also expected in $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-\delta}$. Thus, the Ce-O hybridization effect may contribute that the bond length between Ce^{4+} (or Nd^{3+}) and O^{2-} ions changes with a large amount of doping cations, although the lattice constant and bond length have not been clarified thus far.

The existence of the A peak has been observed in a recent RPES study of CeO_2 by Matsumoto and coworkers.^{14,15} The Ce ion in CeO_2 is nominally tetravalent with no $4f$ electron. They reported that the constant initial state (CIS) spectrum of the A peak has a maximum intensity at ~ 121 eV, though the CIS spectrum of B peak has a maximum intensity at 124.5 eV. This fact indicates that CeO_2 is mixed-valent between the $4f^0$ (Ce^{4+}) and $4f^1\bar{\underline{L}}$ (Ce^{3+}) configurations in the ground states. Here, $\bar{\underline{L}}$ denotes the hole in the valence

band mainly composed of the O 2*p* state. Therefore, we can ascribe the B peak to correspond to the Ce⁴⁺ state and the A peak to correspond to the Ce³⁺ state that exists on a sample surface or near an oxygen defect site. With a simple consideration, the hybridization between the 4*f*⁰ \underline{L} and 4*f*¹ \underline{L}^2 configurations in the final state is expected to nearly equal that between the 4*f*⁰ and 4*f*¹ \underline{L} configurations in the ground state with the average 4*f* electron number of approximately 0.5. The average 4*f* electron number might decrease with Nd³⁺ concentration. Thus, the decrease in the hybridization effect between the Ce 4*f* and O 2*p* states with Nd³⁺ doping can be explained by the decrease in the effective charges of Ce⁴⁺ and O²⁻ ions. In recent years, Mizusaki groups have reported that the electronic conductivity of doped CeO₂ is caused by electron, which result from reduction of Ce ions from Ce⁴⁺ to Ce³⁺. The result of Fig. 3(b) is direct evidence that the Ce⁴⁺ and Ce³⁺ exist at the surface state in Ce_{1-x}Nd_xO_{2-δ}. In order to probe the detailed conduction mechanism of Ce_{1-x}Nd_xO_{2-δ}, the contribution of Nd³⁺ ions must be also clarified in the future study.

In conclusion, we studied the electronic structure of Ce_{1-x}Nd_xO_{2-δ} using RPES. The XAS spectra show that the conduction band is mainly composed of the O 2*p* state hybridized with the unoccupied Ce 4*f* state. The intensity decreases with increasing Nd³⁺ concentration. The RPES spectra show that the hybridization effect between the Ce 4*f* and O 2*p* states in the valence band decreases with increasing Nd³⁺ concentration. This finding indicates that the effective charges of Ce⁴⁺ and O²⁻ ions decrease with Nd³⁺ concentration.

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