Electronic Structure of $\text{BaPr}_{1-x}\text{Yb}_x\text{O}_{3-\delta}$ by Soft-X-Ray Spectroscopy

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The electronic structure of Yb^{3+} -doped BaPrO_3 ($\text{BaPr}_{1-x}\text{Yb}_x\text{O}_{3-\delta}$) has been studied by resonant photoemission spectroscopy and X-ray absorption spectroscopy (XAS). The O 1s XAS spectra exhibit that the conduction band consists of Pr 4*f* and Ba 5*d* states. The valence band is mainly composed of the O 2*p* states hybridized with Pr 4*f* and Pr 5*d* states. The valence band shifts to the lower binding energy side with Yb^{3+} concentration. The Pr 4*f* state has the mixed-valent states of Pr^{4+} and Pr^{3+} . The intensities of Pr^{4+} and Pr^{3+} states rapidly decrease with increasing Yb^{3+} concentration. These results may contribute to the change of charge transfer from O 2*p* to Pr 4*f* states in the ground state with oxygen vacancies and Yb^{3+} substitution.

Keywords: $\text{BaPr}_{1-x}\text{Yb}_x\text{O}_{3-\delta}$, X-ray absorption spectroscopy (XAS), resonant photoemission spectroscopy (RPES), electronic structure, mixed-valent state

1. INTRODUCTION

Perovskite-type oxide BaPrO_3 has an orthorhombic structure (*Pbnm*) with the lattice constant of $a=6.201$ Å, $b=6.173$ Å and $c=8.712$ Å at room temperature [1-5]. The BaPrO_3 is a paramagnetic material with electron conduction in semiconducting region [5]. This material occurs the magnetic transition from paramagnetic phase to antiferromagnetic phase [6-10]. The structural and magnetic properties have been investigated in the research area of solid state physics [1-10]. In the research area of electrochemical, it is known that BaPrO_3 exhibits high electron-proton mixed conduction in intermediate temperature region (600~300°C) when Yb^{3+} ions are substituted into Pr^{4+} site [11-14]. The total conductivity in H_2O atmosphere is over $\sim 10^1$ S·cm⁻¹ in intermediate temperature region [12-14]. The activation energy is estimated to be ~ 0.48 eV [14]. This mixed conductor is expected as electrode material of solid state oxide fuel cells and hydrogen separation membranes [15-16].

In general, the ion conduction is closely related with oxygen vacancies created in the crystal lattice [17-18]. The proton adsorption occurs by exchange of proton and oxygen vacancies or holes created by acceptor substitution. The maximum proton concentration is not over a dopant concentration, because the total amount of oxygen vacancies is limited by the dopant concentration [18]. The high proton conduction is realized on perovskite oxide with rare-earth metal as B^{4+} site of ABO_3 structure such as BaCeO_3 and SrCeO_3 [11,12,19,20]. These proton conductor has the mixed-valent state, which is created by charge transfer from O 2*p* to metal 4*f* states in the ground state [19,20]. Similar situation is also expected in $\text{BaPr}_{1-x}\text{Yb}_x\text{O}_{3-\delta}$. Therefore, understanding the electronic structure of $\text{BaPr}_{1-x}\text{Yb}_x\text{O}_{3-\delta}$ is one of the most important subjects for material design of electrochemical or magnetic device.

In this study, the electronic structures of $\text{BaPr}_{1-x}\text{Yb}_x\text{O}_{3-\delta}$ ($x=0, 0.05$ and 0.10) bulk crystals have been

measured by X-ray absorption spectroscopy (XAS) and high-resolution photoemission spectroscopy (PES). PES and XAS are related directly to the occupied DOS and unoccupied DOS, respectively [21]. From these measurements, the authors probe the changes of valence band, positions of Fermi level (E_F) and mixed-valent state with Yb^{3+} substitution of $\text{BaPrO}_{3-\delta}$ ceramics. In this paper, the authors report that the electron and proton mixed conduction are closely related with the electronic structure.

2. EXPERIMENTAL

The sample powder of $\text{BaPr}_{1-x}\text{Yb}_x\text{O}_3$ ($x=0, 0.05$ and 0.10) has been prepared by a Pechini method using BaCO_3 , $\text{Pr}(\text{NO}_3)_3$, $\text{Yb}(\text{NO}_3)_3$ and citric acid as starting materials. A batch of mixed powder synthesized from homogeneous solution is pressed into disks by a mechanical uni-axial pressing at 200 MPa. The pellets have been sintered at 1400 °C for 10 h, and then furnace cooled. The samples are subjected to a powder X-ray diffraction analysis for the phase identification. Details have been reported in ref. [14].

PES spectra were measured using a soft-X-ray spectrometer installed at the undulator beamline BL-19B in Photon Factory at the High Energy Accelerator Organization (KEK), Japan. Synchrotron radiation was monochromatized using a varied-line spacing plane grating whose average groove density was 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 soft-X-ray spectroscopy system installed at the BL-7.0 in Advanced Light Source at the Lawrence Berkeley National Laboratory, U.S.A. The samples were scraped in situ with a diamond file in a vacuum of 5.0×10^{-10} Torr in order to obtain a clean surface. The energy resolutions of PES and XAS were approximately 0.3 eV and 0.1 eV, respectively, at $h\nu=530$ eV. The energy axis was

calibrated by measuring the photoemission spectrum of 4f core level of Au film.

3. RESULTS AND DISCUSSION

Figure 1 shows the PES spectra as a function of Yb^{3+} concentration for $\text{BaPr}_{1-x}\text{Yb}_x\text{O}_{3-\delta}$. The 0 eV of bottom axis is the position of the Fermi level (E_F). The valence band of $\text{BaPrO}_{3-\delta}$ locates at ~ 3 eV from E_F . This implies that the $\text{BaPrO}_{3-\delta}$ is *n*-type semiconductor since the band gap is approximately 3.2 eV. However, the valence band shifts to the lower binding energy side with Yb^{3+} concentration. In the case of *p*-type material, the E_F locates at near the top of the valence band. Similar situation has been observed in Sc-doped SrTiO_3 [22]. The shifts for $\text{BaPr}_{1-x}\text{Yb}_x\text{O}_{3-\delta}$ correspond to the effect of the doping on the rigid-band model [19,22]. On one hand, the above results indicate that the Yb^{3+} ions are substituted into Pr^{4+} site as acceptor. The spectral shape and band width of the valence band depend on Yb^{3+} concentration. This is considered

Fig. 1 PES spectra in the valence band region as a function of Yb concentration for $\text{BaPr}_{1-x}\text{Yb}_x\text{O}_{3-\delta}$ measured at $h\nu=950$ eV.

Fig. 2 O 1s XAS spectra of $\text{BaPrO}_{3-\delta}$ and $\text{BaPr}_{0.90}\text{Yb}_{0.10}\text{O}_{3-\delta}$.

to be due to the change of the hybridization effect between the O 2p and Pr 4f states. The details will discuss in Fig. 4.

Figure 2 shows the O 1s XAS spectra of $\text{BaPrO}_{3-\delta}$ and $\text{BaPr}_{0.90}\text{Yb}_{0.10}\text{O}_{3-\delta}$. From the dipole selection rule, it is understood that the O 1s XAS spectra of Pr oxides corresponds to transition from O 1s to O 2p character [23-25]. The XAS structures are mainly composed of the O 2p state hybridized with the unoccupied Pr 4f, Pr 5d and Ba 5d states. Therefore, the XAS peaks of ~ 528 eV, ~ 532 eV and ~ 538 eV are estimated to be Pr 4f, Pr 5d and Ba 5d states, respectively [25,26]. Although the peak intensities of Pr 5d and Ba 5d states do not depend on Yb^{3+} concentration, the peak intensity of Pr 4f state is higher in $\text{BaPr}_{0.90}\text{Yb}_{0.10}\text{O}_{3-\delta}$. This indicates that the doped Yb^{3+} ions enter to the Pr 4f and O 2p hybridization states of $\text{BaPrO}_{3-\delta}$ as hole.

In $\text{BaPr}_{0.90}\text{Yb}_{0.10}\text{O}_{3-\delta}$, two structures denoted by the *h* and δ peaks are observed in the band gap energy region. The δ peak is considered to be a defect-induced level of the Pr 4f state, since the structure is located at the bottom of the Pr 4f conduction band. The *h* peak at the top of the valence band is assigned to holes created by Yb^{3+} doping, which is mainly composed of the nonbonding O 2p state in the valence band. Similar structures have been observed in Sc^{3+} -doped SrTiO_3 [27] and Y^{3+} -doped BaCeO_3 [19] with proton conduction.

Figure 3(a) shows the Pr 3d $\rightarrow$ 4f XAS spectrum of $\text{BaPrO}_{3-\delta}$. The overall profile is similar to the XAS

Fig. 3 (a) Pr 3d XAS spectrum of BaPrO_3 . (b) RPES spectra in the valence band region of BaPrO_3 excited at various photon energies shown as A, B, C, and D of Fig. 3(a).

spectra of Pr oxide [25,26]. The vertical bars indicate the selected photon energies for the resonant-PES (RPES) measurements. The peaks A and B correspond to the Pr^{3+} and Pr^{4+} , respectively.

Figure 3(b) show the Pr $3d \rightarrow 4f$ RPES spectra of $\text{BaPrO}_{3-\delta}$ measured at various photon energies of Fig. 3(a). The spectrum D corresponds to the off-resonance, which reflect the O $2p$ DOS in the valence band without the contributions of Pr $4f$ state. The broad structure at -18.5 eV is O $2s$ state. The structure at -8.5 eV in the valence band is Pr $5d$ state hybridized with O $2p$ state since the structure does not exhibit the resonance effect on this excitation energy region. However, the spectrum B measured at the excitation energy of Pr^{4+} state exhibit the strong resonance effect at -5.5 eV (peak β). Furthermore, the spectrum A measured at the excitation energy of Pr^{3+} state exhibit the strong resonance effect at -4.5 eV (peak α). In general, it has been reported that the valence band of Pr compound consists of the mixed-valent state between the $4f^1$ and $4f^2\bar{L}$ configurations in the ground state [25,26]. Here, $\bar{L}$ denotes the hole in the valence band mainly composed

of O $2p$ state. Therefore, we ascribe that the peak β corresponds to the $4f^0$ (Pr^{4+}) state and the peak α corresponds to the $4f^1\bar{L}$ (Pr^{3+}) state that contributes to the charge transfer from the O $2p$ to Pr $4f$ states in the ground state.

Figures 4(a) and 4(b) show the RPES spectra as a function of Yb^{3+} concentration for $\text{BaPr}_{1-x}\text{Yb}_x\text{O}_{3-\delta}$ measured at photon energy corresponding to Pr^{4+} and Pr^{3+} , respectively. The intensities decrease with Yb^{3+} concentration. The $\text{BaPrO}_{3-\delta}$ has the mixed-valent states of Pr^{4+} and Pr^{3+} , which contributes to the oxygen vacancies in the ground state. With a simple consideration, the hybridization effect between the $4f^0\bar{L}$ and $4f^1\bar{L}^2$ configurations in the final state of photoemission is expected to nearly equal that between the $4f^0$ and $4f^1\bar{L}$ configurations in the ground state with the average $4f$ electron number of approximately 0.5. The average $4f$ electron number changes with Yb^{3+} concentration in order to keep the charge neutral condition of $\text{BaPrO}_{3-\delta}$. On the other hand, the total conductivities (σT) of $x=0$, 0.05 and 0.10 have been estimated to be 0.05 S-cm/K, 0.1 S-cm/K and 1.0 S-cm/K, respectively, at 300K [14]. Then, the activation energies of $x=0$, 0.05 and 0.10 are 0.41 eV, 0.37 eV and 0.48 eV, respectively [14]. The decrease of Pr^{3+} state with high binding energy contributes to the hole conduction by Yb^{3+} substitution. Therefore, the mixed-valent state for $\text{BaPr}_{1-x}\text{Yb}_x\text{O}_{3-\delta}$ may be closely related with the high electron (hole)-proton mixed conduction, although the role of Yb $4f$ state at near E_F has not been clarified thus far.

4. CONCLUSION

The authors have studied the electronic structure of $\text{BaPr}_{1-x}\text{Yb}_x\text{O}_{3-\delta}$ ceramics using XAS and PES. The E_F shifts to the valence band side with Yb^{3+} concentration, indicating the effect of acceptor doping on the rigid-band model. The intensity of Pr $4f$ conduction band increases with Yb^{3+} concentration. The valence band is mainly composed of Pr $4f$ and Pr $5d$ hybridized with the O $2p$ state. Furthermore, the valence band has the mixed-valent states of $4f^0$ (Pr^{4+}) and $4f^1\bar{L}$ (Pr^{3+}) in the ground state. This originates to the effect of the charge transfer from the O $2p$ to Pr $4f$ states with Yb^{3+} substitution and oxygen vacancies of BaPrO_3 . The decrease of Pr^{3+} state may activate the hole conduction with Yb^{3+} concentration.

ACKNOWLEDGEMENTS

The authors would like to thank Ms. Chizuko Kudo for her technical and analysis supports.

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Fig. 4 (a) RPES spectra as a function of Yb^{3+} concentration for $\text{BaPr}_{1-x}\text{Yb}_x\text{O}_{3-\delta}$ excited at "B" of Fig. 3(a), which corresponds to Pr^{4+} state. (b) RPES spectra as a function of Yb^{3+} concentration for $\text{BaPr}_{1-x}\text{Yb}_x\text{O}_{3-\delta}$ excited at "A" of Fig. 3(a), which corresponds to Pr^{3+} state.

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(Received August 1, 2014; Accepted December 22, 2014)