

Electronic structure of BaPrO₃-based oxides studied with soft X-ray absorption and emission spectroscopy

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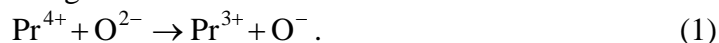
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Introduction

Solid Oxide Fuel Cells (SOFCs) employing proton-conducting oxides as electrolyte are expected as a new generation of SOFCs, which enable low-temperature operation compared with SOFCs using oxide-ion conducting electrolytes. While numerous studies have been devoted to proton-conducting oxides as the electrolytes, there have been fewer reports on the cathode materials for proton-conducting SOFCs (PC-SOFCs). It is considered that protonic and electronic mixed conductivity is an important property for high cathode performance.

In our previous studies, the electrochemical properties of BaPr_{1-x}Yb_xO₃ have been investigated in expectation of proton-hole mixed conductivity [1]. Actually, its proton solubility was found to be rather small, implying poor protonic conductivity in the material. On the other hand, the oxide shows predominant hole conductivity, which increases almost linearly with the dopant concentration, but the conductivity itself is very low. While the observed conduction behaviour appears to follow a classical defect chemistry, we have recently found anomalous electronic structures via X-ray spectroscopy [2]. It has been inferred that both of the unoccupied state which corresponds to a non-bonding O2*p* level doped with hole (O[•]) and the occupied state which corresponds to Pr³⁺ simultaneously decreases in intensity upon doping with Yb. Therefore, it is considered that the two defect species O[•] and Pr³⁺ generate together via an auto-ionization reaction:



In order to further understand the overall picture of the electric transport property as well as electronic structure in the BaPrO₃-based system, we have investigated the impact of oxidation/reduction heat-treatment on soft X-ray absorption spectra.

Experimental

The powders of Ba_{0.95}La_{0.05}PrO₃, BaPrO₃, and BaPr_{0.7}Yb_{0.3}O₃ have been prepared via a citric acid method, and then sintered at 1673K. The samples have been equilibrated at 873K in dry O₂, wet O₂ or dry Ar atmosphere. Soft X-ray absorption spectra have been collected by a total fluorescence method at BL-19B of Photon Factory, KEK.

Results and discussion

Figure 1 shows the O1*s*-2*p* XAS spectra of BaPrO₃ (BP) heat-treated at various conditions of temperature and oxygen partial pressure. A pre-edge peak (A) observed at 534eV has been attributed to a non-bonding O2*p* level doped with hole, O[•], which generates

via the above-mentioned auto-ionization reaction. The density of the hole state (A) decreases with decreasing the oxygen partial pressure of heat-treatment, which suggests the annihilation of the holes and formation of oxide ion vacancies upon reduction.

The similar measurements have been performed on $\text{BaPr}_{0.7}\text{Yb}_{0.3}\text{O}_3$ (BPY30) as shown in Fig. 2. In the $\text{O}1s\text{-}2p$ XAS spectra of BPY30, a shoulder (B) is observed at the low energy side of the peak (A). Since the hole conductivity of $\text{BaPr}_{1-x}\text{Yb}_x\text{O}_3$ increases with x [1], it is deduced that the unoccupied state (B) corresponds to the electron holes introduced by Yb^{3+} -doping. Comparing the spectra of the samples after different heat-treatments, it is found that the hole densities of both (A) and (B) decrease upon the decrease in the oxygen partial pressure. As a result, the density of the hole state (B) almost disappears, which is consistent to the observation that the hole conductivity decreases upon reduction accompanied by the formation of oxide ion vacancy [1]. This confirms that the hole state (B) is responsible for the observed electric conduction.

Figure 3 shows the $\text{Pr}3d\text{-}4f$ XAS spectra of BPY30 samples after heat-treatments. In the $\text{Pr}\text{-}M_5$ edge region, the peak (a) and (b) are considered to correspond to Pr^{3+} and Pr^{4+} , respectively. Upon reduction of the sample, the intensity of the Pr^{3+} peak slightly increases. This behaviour is consistent to the effect of heat-treatment on the $\text{O}1s\text{-}2p$ XAS spectra from the viewpoint of decrease in the hole density upon reduction, while the impact on the $\text{Pr}3d\text{-}4f$ XAS spectra is rather small compared with $\text{O}1s\text{-}2p$ spectra. The above observations indicate that the charge compensation for red-ox reaction and acceptor(Yb)-doping is mostly made by oxygen rather than praseodymium.

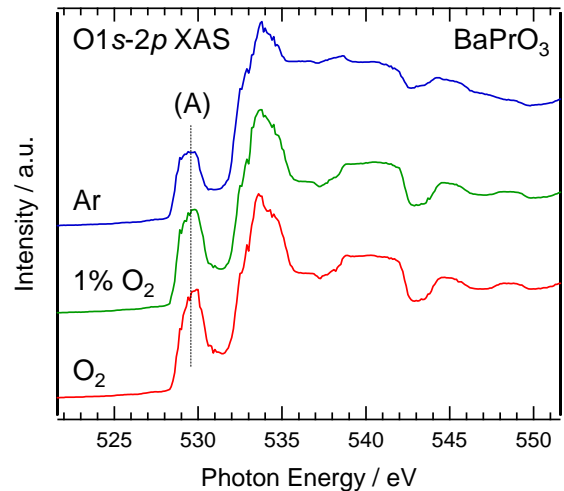


Fig. 1: $\text{O}1s\text{-}2p$ XAS spectra of BaPrO_3 .

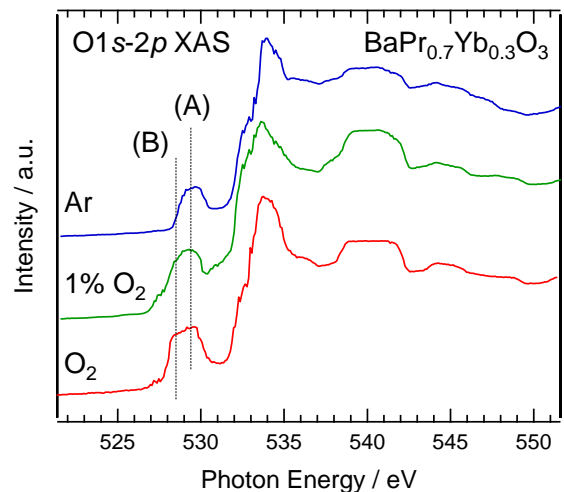


Fig. 2: $\text{O}1s\text{-}2p$ XAS spectra of $\text{BaPr}_{0.7}\text{Yb}_{0.3}\text{O}_3$.

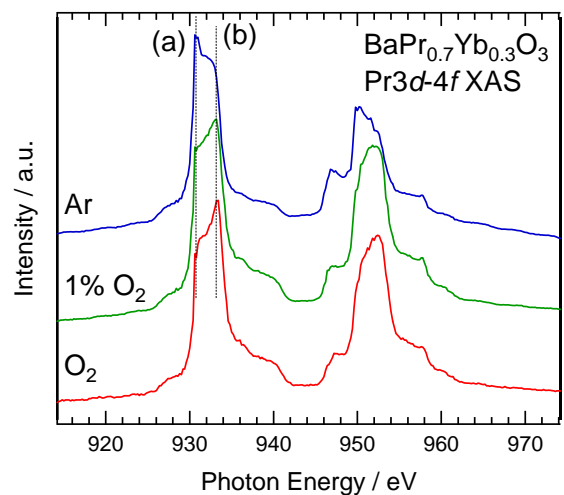


Fig. 3: $\text{Pr}3d\text{-}4f$ XAS spectra of $\text{BaPr}_{0.7}\text{Yb}_{0.3}\text{O}_3$.

Reference

- [1] S. Mimuro et al., Solid State Ionics 178, 641 (2007).
- [2] S. Yamaguchi et al., Activity Report of Synchrotron Radiation Laboratory 2008.