

Electronic structure and auto-ionization process of ion-electron mixed-conductor

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1 Introduction

Solid Oxide Fuel Cell (SOFC) is one of the most promising devices for efficient energy conversion. In order to lower the operating temperature, proton-conducting oxides have attracted much attention as electrolyte of SOFCs. BaZrO₃-based perovskite oxides are most promising materials for the electrolytes due to their good chemical stability and high proton conductivity. On the other hand, the electrode materials for such proton-conducting SOFCs have not been well studied. In order to provide larger effective electrode reaction area and high electrode performance, it is required to develop materials with proton-electronic mixed conduction.

For developing such mixed-conducting materials, the electrochemical properties have been investigated on BaZrO₃ doped with Pr, which takes a mixed valence state of Pr^{3+/4+}. It was found that the electric conduction in oxidizing atmosphere is dominated by electron hole, while in reducing atmosphere, protonic conduction prevails in addition to hole conduction. Both of the hole and proton conductivity increase with the Pr concentration in the perovskites. However, the dependence of the both conductivity on the Pr concentration is nonlinear, showing a cubic dependency.

In this study, soft X-ray Absorption Spectroscopy (XAS) has been employed to observe the unoccupied density of states around the Fermi level, which is crucial to the hole conduction.

2 Experiment

The powders of BaZr_{1-x}Pr_xO₃ (0 ≤ x ≤ 0.6) have been prepared via a citrate method, and then sintered at 1873K. Prior to the XAS measurements, the samples have been equilibrated at 873K in dry O₂ atmosphere. Soft X-ray absorption spectra have been collected by a total fluorescence method at BL-19B of Photon Factory, KEK.

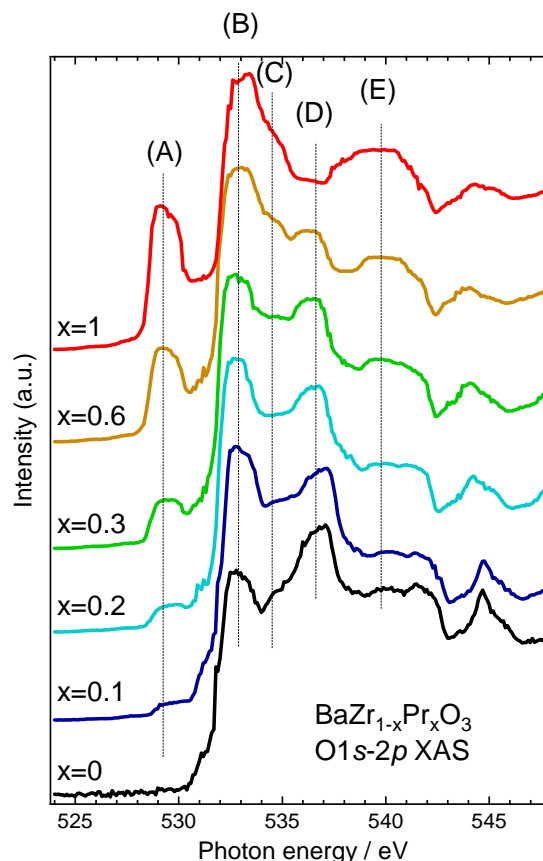
3 Results and Discussion

Figure 1 shows the O1s-2p XAS spectra of BaZr_{1-x}Pr_xO₃. The spectrum of BaZrO₃ shows a main absorption edge peak (B) at 533eV with no pre-edge peaks. The feature (D) significantly attenuates upon increase in the Pr concentration, x, which indicates the origin being Zr4d orbital. On the other hand, the features (C) and (E) grow due to the contribution from Pr 4f orbital.

More importantly, a pre-edge peak (A) appears upon Pr-doping, and the intensity increases with x. Undoped BaPrO₃, which is essentially a p-type conductor [1], shows the identical pre-edge peak as found in Fig. 1 and previously reported [2]. As previously discussed [2], this

pre-edge peak is considered to originate from the unoccupied state in O2p orbital, that is, holes localized at oxide ions. Therefore, the hole conductivity in BaZr_{1-x}Pr_xO₃, which increases with x, is regarded as closely related to the unoccupied density of states (A).

The intensity of the pre-edge peak (A) linearly increases with x. On the other hand, the hole conductivity, σ_h, has been found in a cubic correlation with x as previously mentioned; σ_h ∝ x³. The difference in the dependence on x between the density of the hole state (A) and the hole conductivity indicates that the apparent mobility of the holes is strongly dependent on the Pr concentration. This behaviour suggests that the electron holes, which are located on the oxide ion, are strongly correlated with the negative electronic defects, i.e., Pr³⁺, via the auto-ionization reaction: Pr⁴⁺ + O²⁻ → Pr³⁺ + O⁻.

Fig. 1: O1s-2p XAS spectra of BaZr_{1-x}Pr_xO₃.

References

- [1] S. Mimuro et al., Solid State Ionics 178, 641 (2007).
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