

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

Shu Yamaguchi¹, Tohru Higuchi², Yukiko Oyama¹, Shogo Miyoshi¹, Mao Tamaru¹

1 Department of Materials Engineering, The University of Tokyo

2 Department of Applied Physics, Tokyo University of Science

Introduction

Solid Oxide Fuel Cell (SOFC) is very promising device for efficient energy conversion. However, the operating temperature of conventional SOFCs with ZrO₂-based electrolyte is as high as 1000 °C, which involves some problems such as long-term stability and limitation of applicable materials. In order to lower the operating temperature, proton-conducting oxides have attracted much attention as electrolyte of SOFCs, since the activation energy of proton conduction in those oxides is generally lower than that of oxide-ion conduction. Among those oxides, 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 resulting high electrode performance, it is required to develop materials with proton-electronic mixed conduction.

In order to develop 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. The capability of incorporating protons is facilitated by reduction of Pr⁴⁺ to Pr³⁺, which works as an acceptor to form oxygen vacancy and also protonic defect of OH₀[•]. Both of the hole and proton conductivity in oxidizing and reducing atmosphere, respectively, 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.

For understanding the conduction behaviour, it is essential to give insight into the electronic structure. 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.

Experimental

The powders of BaZr_{1-x}Pr_xO₃ (0 ≤ x ≤ 0.5) have been prepared via a citric acid method, and then finally sintered at 1873K. The sintered samples have been confirmed via XRD to crystallize in a single phase of a perovskite-type structure. 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.

Results and discussion

Figure 1 shows the $O1s-2p$ XAS spectra of $BaZr_{1-x}Pr_xO_3$. The spectrum of $BaZrO_3$ shows a main absorption edge peak (B) at 533eV with no pre-edge peaks. The several features intensify or attenuate upon increase in the Pr concentration, x , with the main edge energy being constant. The feature (D) significantly attenuates, which indicates the origin being Zr $3d$ 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 $BaPrO_3$, 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 $BaZr_{1-x}Pr_xO_3$, which increases with x , is regarded as closely related to the unoccupied density of states (A).

In Fig. 2, The normalized intensity of the pre-edge peak (A) is plotted against the Pr concentration, x . It is well demonstrated that the density of the hole state 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; $\sigma_h \propto x^3$. 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., Pr^{3+} , via the auto-ionization reaction:

$$Pr^{4+} + O^{2-} \rightarrow Pr^{3+} + O^{-}$$

Reference

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

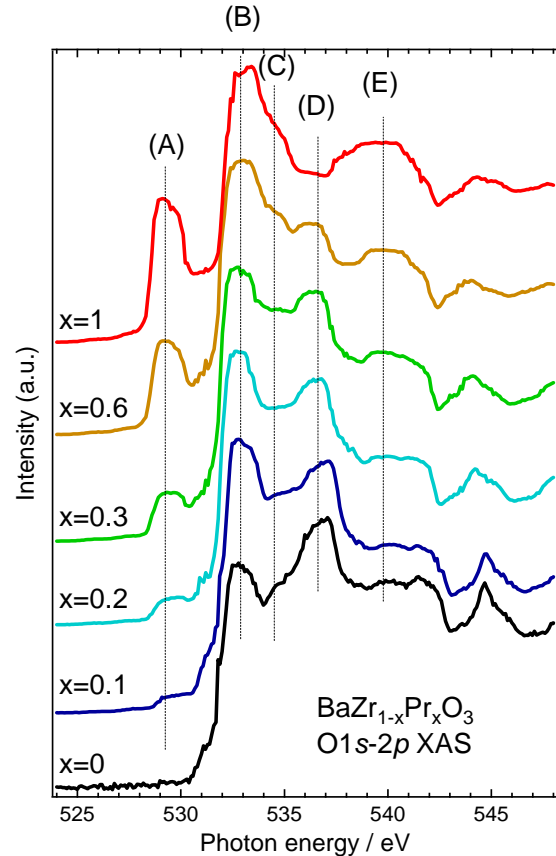


Fig. 1: $O1s-2p$ XAS spectra of $BaZr_{1-x}Pr_xO_3$.

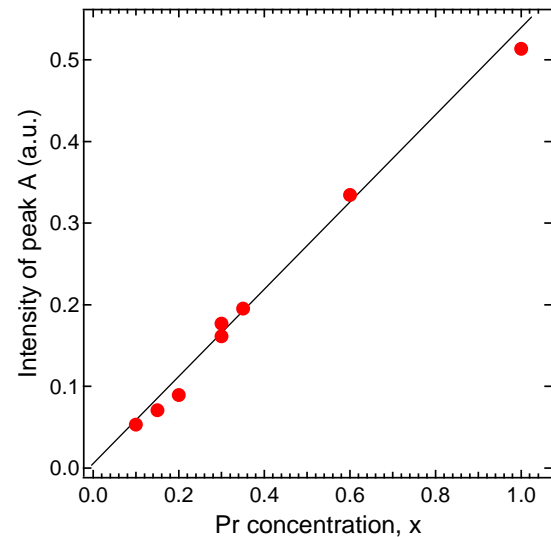


Fig. 2: Intensity of the peak (A) as a function of x .