# Electronic structure and auto-ionization process of

## ion-electron mixed-conductor

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#### Introduction

There have been considerable efforts to reduce operating temperature of Solid Oxide Fuel Cells (SOFCs). In this regard, proton conducting-SOFCs ( $H^+$ -SOFCs) have attracted much attention due to potential performance at low temperatures (~600°C) [1,2]. While most of researches related to  $H^+$ -SOFCs have focused on development of electrolyte materials, investigations of electrode materials have been rather scarce. Especially, only few reports can be found on mixed protonic-electronic conductors, which will facilitate sufficient electrode performance in  $H^+$ -SOFCs due to extended reaction area [3,4].

A partial substitution of transition metal cations for Zr in BaZrO<sub>3</sub>, which is a parent phase of typical proton-conducting perovskite oxides, is expected to introduce electronic conductivity to realize mixed protonic-electronic conduction since transition metal cations that take multiple valence states can provide electron/hole-conduction pathway. After preliminary experiments, the authors found a significant solubility of Fe in BaZrO<sub>3</sub>, which is rather larger than those of the other first-row transition elements. Here the authors propose that the heavily Fe-doped BaZrO<sub>3</sub> may serve as a bi-percolation system of proton and electron mixed conductivity. The present study is aimed at demonstrating unique features of such a bi-percolation system on B-sublattice of ABO<sub>3</sub> perovskite structure via systematic study on electronic structure, electric conductivity, oxygen nonstoichiometry and hydration reaction of  $BaZr_{1-x}Fe_xO_3$ . 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**

Powders of  $BaZr_{1-x}Fe_xO_3$  have been synthesized via a citrate process and are sintered at 1300~1500<sub>o</sub>C. For XAS analysis, the samples have been heat-treated at 800<sup>o</sup>C for 10h in dry O<sub>2</sub> or humidified 1vol% H<sub>2</sub>-Ar atmospheres. XAS measurements on O-*K* edge have been performed at BL-19B of the Photon Factory, KEK. The electric conductivity measurements have been made on sintered pellets by two terminal ac-impedance method as a function of temperature, *P*O<sub>2</sub> and dopant concentration.

## **Results and discussion**

The O K-edge XAS spectra of  $BaZr_{1-x}Fe_xO_3$  heat-treated in dry O<sub>2</sub> atmosphere are shown in Fig. 1. The spectrum of  $BaZrO_3$  shows a main absorption edge at 532eV with no pre-edge peaks. On the other hand, a pre-edge absorption (A) and (B) appears upon

Fe-doping, and the intensity increases with the Fe content, x. The pre-edge absorption is considered to correspond to unoccupied state introduced by Fe. The feature (A) can be attributed to hole state introduced by Fe<sup>3+</sup>-doping at the top of the valence band which is composed of nonbonding O2*p* state, while the feature (B) can be attributed to O2*p* state hybridized with Fe3*d*. The intensity of the feature (A), which is considered to reflect the hole concentration, increases in a almost linear correlation with *x*.

Figure 2 shows the Arrhenius plot of the total electric conductivity for  $BaZr_{1-x}Fe_xO_3$ in dry O<sub>2</sub> atmosphere. The electric impedance of the  $BaZr_{1-x}Fe_xO_3$  specimens yields Nyquist plots with a single semi-circle having no low-frequency spikes, which signify electronic conduction rather than ionic one. Since the total conductivity has been found positively dependent on oxygen partial pressure, the electric conduction in oxidizing atmospheres is considered as of p-type. While the hole conductivity increases with *x* as found in Fig. 2, the dependence is significantly non-linear, which is contrasted by the density of the hole state almost linearly dependent on *x* (Fig. 1). These observations indicate that the apparent mobility of the electron holes is suppressed in the lightly doped compositions, *x*=0.1 and 0.2, suggesting that the hole conduction is controlled by a site-percolation mechanism in heavily doped compositions.



Fig. 1. O *K*-edge XAS spectra of  $BaZr_{1-x}Fe_xO_3$  heat-treated at 800°C in dry O<sub>2</sub>. Broken lines indicate the states of (A) hole and (B) O2*p* hybridized with Fe3*d*, respectively.



Fig. 2. Arrhenius plot of the total electric conductivity for  $BaZr_{1-x}Fe_xO_3$  in dry  $O_2$  atmosphere.

## References

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