

## Electronic structure of BaPrO<sub>3</sub>-based oxides studied with soft X-ray absorption and emission spectroscopy

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### Introduction

Proton-conducting oxides are expected as the electrolyte material of Solid Oxide Fuel Cells (SOFCs) of future generation, which are operated at low-temperature. Compared with numerous studies on proton-conducting oxides as the electrolytes, there have been limited numbers of studies on the cathode materials for proton-conducting SOFC (PC-SOFC). One of the most important properties for the cathode materials is proton-hole (or electron) mixed conductivity, which can extend the effective site of electrode reaction.

So far, we have studied the electrochemical properties of BaPr<sub>1-x</sub>Yb<sub>x</sub>O<sub>3</sub> in expectation of proton-hole mixed conduction [1]. However, it has been revealed that the proton solubility of BaPr<sub>1-x</sub>Yb<sub>x</sub>O<sub>3</sub> is quite small. On the other hand, the oxide shows predominant hole conductivity, which increases almost linearly with the dopant concentration. It is worthwhile to note that the apparent hole mobility, which is simply estimated based on the carrier concentration equivalent to the acceptor one, is rather low. While the observed conduction behavior appears to follow a classic defect-chemistry, we have recently found anomalous electronic structures via X-ray absorption spectroscopies (XAS). Here we report the results of XAS, emphasizing a strong correlation between trivalent Pr and hole/proton.

### Results and discussion

The powders of BaPrO<sub>3</sub> have been synthesized via a citrate process, and then sintered at 1673 K. The sintered bodies have been served for XAS and photoelectron spectroscopy (XPS). Figure 1(B) shows the resonant XPS spectra around the Fermi level of BaPrO<sub>3</sub>, which reflects the occupied density of state around the valence band. The excitation energies have been selected based on the Pr3d-4f XAS spectrum, which is shown in Fig. 1(A). The excitation energy (d) in Fig. 1(A) is regarded to involve no resonant effect, and it is therefore considered that the XPS spectrum (d) in Fig. 1(B) corresponds to the total density of states of the valence band.

In the XPS spectra (b) and (c) in Fig. 1(B), a clear resonance effect is observed at a binding energy of -6.0 eV. Because the excitation energies (b) and (c) shown in Fig. 1(A), which cause the main absorption peak, may correspond to the tetravalent state of Pr ion, the density of state around -6.0 eV can be attributed to Pr<sup>4+</sup> state. In the

XPS spectrum (a), on the other hand, a strong resonance is acknowledged at -4.2 eV. The small feature in the XAS spectrum (Fig. 1(A)) corresponding to the excitation energy (a) is considered to originate from trivalent Pr state. Therefore, the density of state around -4.2 eV can be attributed to Pr<sup>3+</sup> state. In the previous report [2], we suggested the formation of hole on oxygen site, which has been deduced from a pre-edge peak in O1s-2p XAS spectra. Summarizing these results, one can conclude the formation of Pr<sup>3+</sup> and O<sup>-</sup> via an auto-ionization reaction, which are strongly attracted to each other.

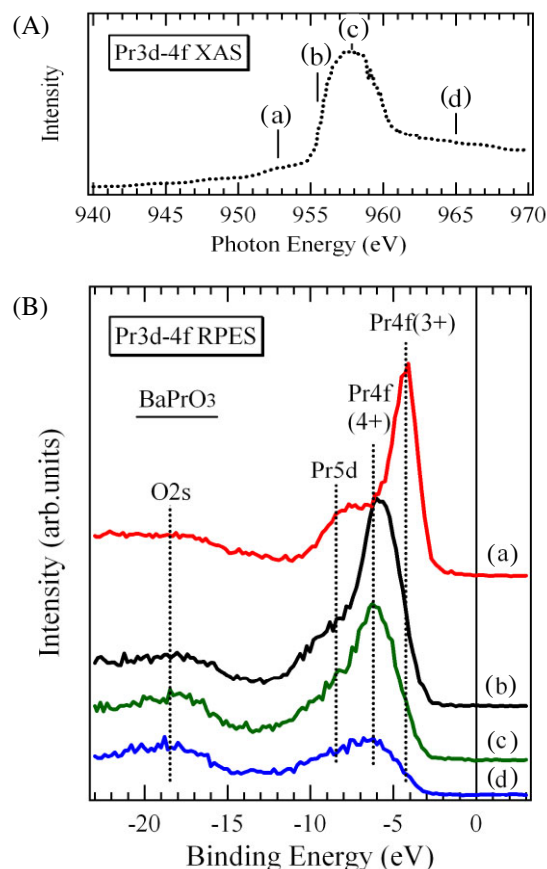


Fig. 1. Pr3d-4f XAS (A) and RPES (B) spectrum of BaPrO<sub>3</sub>.

### References

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