

Bond Percolation Conductivity in Heavily Fe-doped BaZrO₃ and its application in H⁺-SOFC

(Feを高濃度にドーピングしたBaZrO₃におけるボンドパーコレーション伝導とH⁺-SOFCへの応用)

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Fe-doped BaZrO₃ (BaZr_{1-x}Fe_xO_{3-δ}) has been explored as a percolation conductor to demonstrate percolation conduction in single phase system, and to provide a guide principle for designing a mixed protons/electron-holes conductor (H⁺-MIEC). The study has been focusing on the evaluation of electronic structure and electrical transport properties to demonstrate the percolation conduction. Finally, new percolation model for single phase conductor is proposed, and the guide principle of H⁺-MIEC is established as bi-percolation conductor.

The samples of BaZr_{1-x}Fe_xO_{3-δ} ($x=0-0.9$) are successfully synthesized by Pechini process. It exhibits the formation of three solid solutions of Zr-rich cubic ($0 \leq x \leq \sim 0.45$), and Fe-rich rhombohedral and tetragonal phases ($\sim 0.6 \leq x \leq 1.0$). The solid solution boundary of rhombohedral and tetragonal is not clearly separated, because of limited data sets, but the formation of rhombohedral is clearly confirmed by high temperature XRD.

The electronic structure of unoccupied energy state for BaZr_{1-x}Fe_xO_{3-δ} has been studied by an X-ray Absorption Spectroscopy (XAS) to understand electronic defect formation reactions in Fe-doped BaZrO₃. The analysis of Fe *L*-edge XAS spectra suggests that valence state and ground state of Fe under oxidizing atmosphere are Fe³⁺ and 3d⁵L (L denotes a ligand-hole), respectively. The formation of two pre-edge features by Fe doping is observed in O *K*-edge

XAS spectra. One of these features is related to unoccupied $O2p$ - $Fe3d$ hybridizing state while the other is assigned to an acceptor level composed of unoccupied nonbonding $O2p$ state, the latter of which split into two different fine structures of localized holes in chained FeO_6 octahedra and those in isolated FeO_6 octahedron (O^- bridging Fe^{3+} and Zr^{4+}). The intensity of the acceptor level is very sensitive to both the Fe concentration and the partial pressure of oxygen gas, P_{O_2} , both of which modulate the acceptor concentration through defect chemical reaction. The present results suggest surprising conclusion that oxidation state of Fe-doped $BaZrO_3$ is governed by the valence state of oxide ions between O^{2-} to O^- with the fixed valence state of Fe^{3+} and no signature of the formation of Fe^{4+} is observed.

The electronic band structure of $BaZr_{1-x}Fe_xO_{3-\delta}$ is studied using a combined technique of XAS and Resonant X-ray Emission Spectroscopy (RXES). $O2p$ RXES spectra are analyzed to understand the electronic structure of valence band. The nonbonding $O2p$ state is located at a valence band maximum (VBM), and $O2p$ - $Fe3d$ hybridizing level and $O2p$ - $Zr4d$ hybridizing level are arranged in lower energy side in the valence band. $Fe3d$ RXES spectra analysis provides that the optical band gap is formed by the energy separation between nonbonding $O2p$ state on VBM and $O2p$ - $Fe3d$ hybridizing level on a conduction band minimum (CBM), and is ~ 2 eV.

Electrical transport properties of $BaZr_{1-x}Fe_xO_{3-\delta}$ have been investigated to understand conduction mechanism and to demonstrate percolation conduction. The electrical conductivity measurement suggests that p -type conduction prevails under oxidizing atmosphere, and the hole conduction exhibits a nonlinear Fe concentration dependence associated with abrupt change of the apparent activation energy. In addition, a thermoelectric power measurement shows an abrupt increase of hole mobility at $x=0.3$ in $BaZr_{1-x}Fe_xO_{3-\delta}$, in spite of linear increase of hole

concentration confirmed by XAS analysis. The results are attributed to percolation conduction, and it is explained by a newly proposed three dimensional (3-*D*) simple cubic bond percolation conductivity model. In the new percolation model, the charge carrier donation effect should be considered, since the carriers are formed by chemical doping. Holes are strongly localized on FeO₆ octahedron surrounded by ZrO₆ matrix with a large hole formation energy, if Fe concentration is lower than percolation threshold. On the other hand, the holes can migrate through FeO₆ octahedra network chain with small energy, if Fe concentration is higher than the percolation threshold. An electromotive force measurement suggests that the occupation of hydroxyl group, OH, to oxygen vacancies formed by Fe doping is not favored. Proton conductivity can be enhanced by a co-doping of Y³⁺ with Fe³⁺ under keeping of high hole conductivity, and the proton conductivity approaches to bulk proton conductivity of Y³⁺-doped BaZrO₃, when Y concentration (*y*) is higher than 0.2 in BaZr_{0.7-y}Fe_{0.3}Y_{*y*}O_{3- δ} . From this research, single phase percolation conductor and bi-percolation conductor are clearly demonstrated.