

## LOCAL DISTORTION BY DOPANTS AND PERCOLATION CONDUCTIVITY IN OXIDES

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The chemical doping is a typical method to modulate the physical and chemical properties of oxides and other ionic solids and is often applied to emerge ionic conductivity by introducing ionic defects such as oxygen vacancy with suppressed electronic defects. However, those chemical dopants, which can also be categorized as an ionic defect, attract mobile species and work as a trap center for mobile ionic and electronic defects. This study is motivated to understand the origin of such interaction by DFT calculation and Raman scattering spectroscopy. The percolation conductivity, which appears as a result of such strong interaction between dopants and mobile carriers, is further discussed with emphasis on the crucial role of local distortion and its dynamic contributions.

The present study consists of two parts: The DFT simulation and Raman spectroscopy measurements on tetravalent ion-doped CeO<sub>2</sub> to estimate the local distortion around the dopant ions. In the second part, we discuss percolation conductivities of proton and holes in proton-conducting perovskite oxides based on electrochemical measurements and the DFT simulation.

Pure CeO<sub>2</sub> with cubic fluorite structure, known as a host material for excellent oxide ion conducting electrolyte with relatively high partial electronic conductivity in reducing conditions, shows a sharp and single triply-degenerated F<sub>2g</sub> peak in Raman spectroscopy owing to the crystal symmetry. Upon chemical doping of acceptor dopants, CeO<sub>2</sub> starts to show multiple broad peaks slightly higher wave number to the F<sub>2g</sub> main peak, usually attributed to oxygen vacancy-induced local vibrational modes. There is, however, controversy left on the assignment of these defect induced peaks because observed broad dopant induced peaks never agree with the finitely split peaks estimated by DFT calculation.

In the present study, we employed CASTEP code using GGA-PBE functional for DFT simulation and made careful calculations: At first, the stable local structure of doped and undoped CeO<sub>2</sub> was estimated by a structural relaxation concerning local distortion and energy, and Raman spectra were simulated by calculating scattering cross section. The present results on the DFT calculation suggest that the origin of dopant-induced peaks is due to a broken local symmetry by the presence of foreign atoms of dopants, but the intensity is determined by the extent of local distortion and extended relaxation length by the difference of ionic size of dopant and the matrix Ce<sup>4+</sup> ions (1). Large distorted shells are isolated each other at lower concentration regime while overlapping begins at a relatively low concentration around 1-2% in case of cubic fluorite CeO<sub>2</sub> phase owing to an extended relaxation length of local distortion. When all dopant ions are isolated, overall properties are governed by the matrix properties. In contrast, the stress shell accommodating dopant ion begin contributing to the macroscopic physical and chemical properties above a critical concentration. The overlapping shell contributes to the broadening of the Raman F<sub>2g</sub> and dopant related peaks (2). The stress shell mentioned above serves as an attracting or repulsive center for mobile ionic and electronic defects. We find good examples, such as oxide ion conductivity in acceptor-doped CeO<sub>2</sub>( ) and holes and proton conductivities in acceptor-doped perovskite oxides ( 3, 4 ). In the latter system, a transition from isolated traps to the percolation conductivity has been clearly observed, and discussion on local distortion is developed on the basis of both experimental and theoretical results ( 5 ).

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