Competing f-electron localization mechanisms in rare earth cubic fluorites

T. Kolodiazhnyi[1,*], P. Tipsawat[2], T. Charoonsuk[3], S. Jungthawan[2], N. Vittayakorn[3]

[1]*National Institute for Materials Science, Tsukuba, 305-0044, JAPAN*
[2]*School of Physics, Suranaree University of Technology, Nakhon Ratchasima, 30000, THAILAND*

[3]*Department of Chemistry, King Mongkut's Institute of Technology Ladkrabang, Bangkok, 10520, THAILAND*

[*]*corresponding author, E-mail: kolodiazhnyi.taras@nims.go.jp*

Abstract

4f electron localization and transport in n-type PrO_2 and CeO_2 has been traditionally treated in terms of the Holstein small polaron (SP) model. According to the SP model, electron mobility at sufficiently high temperature ($T > 1/2\theta$, θ being the Debye temperature) is determined by the thermally activated hopping of self-trapped electrons between the neighbor Pr(Ce) sites. The SP scenario is applicable when the SP band width, $2J_P$, is equal to or smaller than the (longitudinal) optical phonon energy. The first-principles calculations indicate that the rigid lattice 4f electron band is sufficiently wide (~1.4 eV) and, once it is partially populated, it should warrant itinerant electron (i.e., metal-type) transport in n-type ceria. This, however, is not confirmed by experimental results where conductivity diverges to zero at low temperatures.

In a real-case ceria, imperfections in the form of intrinsic defects and donors/acceptors contribute to the disorder of the otherwise ideal crystalline lattice. According to Anderson, when the disorder strength becomes comparable with the band-width, localization of itinerant charge carriers will take place even in the absence of the SP effects. From the experimentalist's viewpoint, the main question is: What is the dominant driving force for electron localization in ceria: Is it the SP electron-lattice interaction, or is it the disorder-induced Anderson localization?

In this contribution we examine the role of different donor dopants (e.g., Nb^{5+}, Ta^{5+} and W^{6+}) on the electron conductivity of ceria with a main goal to distinguish between the Ce^{3+}-lattice and Ce^{3+}-defect interactions. While the electron-phonon interaction is strong, we demonstrate that the Coulomb interaction between the donor defects and the $4f^1$ electrons play a dominant role in the electron localization in n-type ceria.

Keywords: 4f-electrons, ceria, Anderson localization, small polarons.