# Highlights

Oxides —2017

## Effects of Dopant Ionic Radius on Cerium Reduction in Epitaxial Cerium Oxide Thin Films

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The role of trivalent rare-earth dopants on the cerium oxidation state has been systematically studied by in situ photoemission spectroscopy with synchrotron radiation for 10 mol% rare-earth doped epitaxial ceria films (Fig.1). It was found that dopant rare-earths with smaller ionic radius foster the formation of $Ce^{3+}$ by releasing the stress strength induced by the cation substitution (Fig.2). With a decrease of the dopant ionic radius from $La^{3+}$ to $Yb^{3+}$, the out-of-plane axis parameter of the crystal lattice decreases without introducing macroscopic defects. The high crystal quality of our films allowed us to comparatively study both the ionic conductivity and surface reactivity ruling out the influence of structural defects.
The measured increase in the activation energy of films and their enhanced surface reactivity can be explained in terms of the dopant ionic radius effects on the $Ce^{4+} \rightarrow Ce^{3+}$ reduction as a result of lattice relaxation. Such findings open new perspectives in designing ceria-based materials with tailored properties by choosing suitable cation substitution.

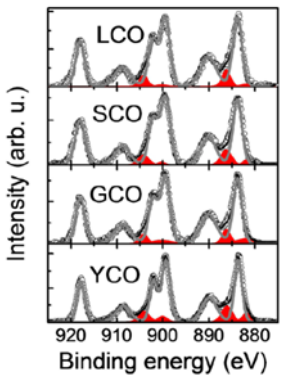


Fig.1: Ce 3d core level photoemission spectra for RECO thin films (RE=Yb, Gd, Sm, La). The solid gray line refers to the sum of all $Ce^{4+}$ fit components and the red filled areas to the sum of all $Ce^{3+}$ fit components.

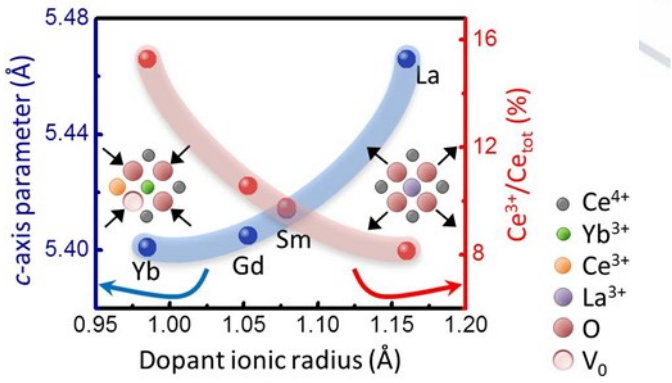


Fig.2: Dopant ionic radius dependence of the c-axis parameter (blue balls) and the $Ce^{3+}$ concentration (red balls) calculated from the corresponding red filled areas in Fig.1.