# Highlights

## RESEARCH AREA 1 - Superconductors and Innovative materials for Energy and Environment - 2024

### Unveiling the local structure of doubly doped $CeO_2$: a synchrotron X-ray pair distribution function study

A. Martinelli[1], S. Massardo[2], C. Artini[2,3], M. M. Carnasciali, M. Pani[1,2]

[1]CNR-SPIN Institute of Superconductors, Innovative Materials and Devices, UOS-Genova, Genova, Italy
[2]Department of Chemistry and Industrial Chemistry, University of Genova, Genova, Italy
[3]CNR-ICMATE Institute of Condensed Matter Chemistry and Technologies for Energy; Genova, Italy

JOURNAL OF MATERIALS CHEMISTRY A

The structural evolution of doubly rare-earth (RE) doped ceria systems with formula $(Ce_{1-x}RE_x)O_{2-x/2}$ (RE = Nd/Dy, Nd/Tm, Gd/Sm) was investigated across a wide compositional range (x = 0.05–0.60). Although optimal ionic conductivity typically occurs at x = 0.10–0.20, higher doping levels were examined to clarify structural changes affecting material performance.
Samples were synthesized via co-precipitation, ensuring high homogeneity. Structural analysis combined synchrotron X-ray powder diffraction (XRPD), Rietveld refinement, and pair distribution function (PDF) analysis to probe both long- and short-range structural properties. The bond valence sum (BVS) method was applied to assess structural stability and ionic transport pathways (Fig. 1).
At low doping ($x \leq 0.30$), all systems exhibit a single-phase fluorite structure ($Fm\bar{3}m$), characteristic of $CeO_2$. At higher x, a secondary $Ia\bar{3}$ phase (typical of $RE_2O_3$) emerges, indicating phase coexistence driven by oxygen vacancies formed when $Ce^{4+}$ is replaced by $RE^{3+}$. Lattice parameters initially increase with x, then deviate as strain accumulates and phase separation begins.
Chemical substitution reduces crystallite size and increases both static (bond length variation) and dynamic (atomic displacement) disorder. BVS analysis shows significant structural strain beyond x = 0.30, promoting instability and cation segregation: Ce remains in the fluorite structure, whereas RE ions concentrate in the $Ia\bar{3}$ one.
PDF analysis reveals that even at low doping, the local structure deviates from the ideal fluorite model. A two-phase ($Fm\bar{3}m$ + $Ia\bar{3}$) description better captures short-range order (<10 Å), indicating nanoscale fluctuations resembling both $CeO_2$ and $RE_2O_3$ environments. These are interpreted as vacancy-related defect clusters rather than true phase separation. Two regimes of disorder are observed: a linear increase for $x \leq 0.30$, followed by saturation due to phase coexistence. Locally, RE–O and RE–RE distances decrease with increasing x due to Coulombic interactions around oxygen vacancies (Fig. 2). Importantly, non-conductive defect clusters form even at low substitution, limiting ionic conductivity. However, double substitution extends fluorite stability and improves high-temperature conductivity, highlighting its potential for solid oxide cell applications.

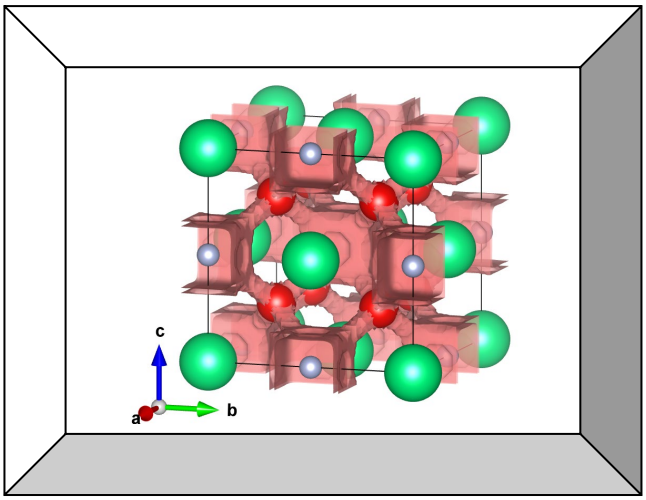


Fig. 1: Bond valence isosurface of $O^{2-}$ in $CeO_2$; interstitial sites (grey spheres) are located at the 24*e* Wyckoff site.

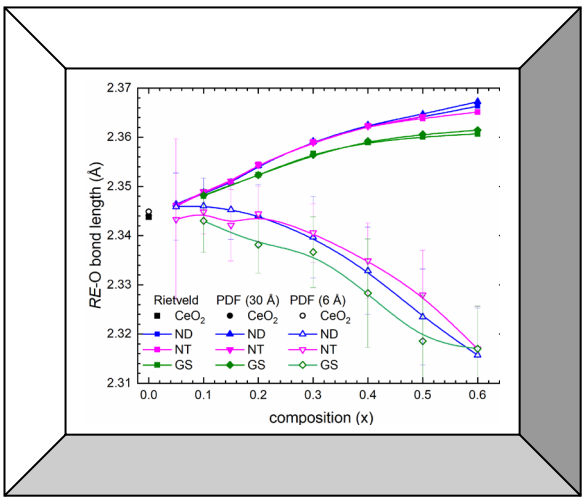


Fig. 2: RE–O bond lengths plotted as a function of composition as obtained by Rietveld refinement and PDF fittings up to distance ranges 6.15 and 30 Å.

Consiglio Nazionale delle Ricerche
SPIN