

# Influence of lanthanum doping on the structure and transport properties of CeO<sub>2</sub>

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La<sub>x</sub>Ce<sub>1-x</sub>O<sub>2-x/2</sub> materials are oxide and/or proton conductors depending on the La-content and they are of interest for numerous electrochemical applications at high temperatures, including membranes for hydrogen separation and fuel cell electrolytes. Samples with low La-content exhibit ( $x \leq 0.4$ ) crystallize with cubic fluorite type structure; while for  $x > 0.4$  the structure is still unclear. The crystal structure of these materials is still unknown, some authors reported that the materials exhibit fluorite type structure in the whole compositional range. However, another authors reported a pyrochlore type structure for  $x \geq 0.5$ . The stabilization of the fluorite or pyrochlore type structure depends mainly on the oxygen sublattice and the vacancy ordering<sup>1</sup>.

In this contribution, La<sub>x</sub>Ce<sub>1-x</sub>O<sub>2-δ</sub> ( $0 < x \leq 0.7$ ) materials are prepared by the freeze-drying precursor method and the sintering conditions have been optimized to obtain dense ceramic samples. A complete structural characterization has been carried out by X-ray powder diffraction and scanning electron microscopy. The average structure determined by conventional XRD indicates that the materials are single fluorite compounds for  $x \leq 0.6$ . However, the local structure determined by combined electron diffraction and HRTEM is more complex. The SAED patterns reveal diffuse scatterings for  $x \geq 0.5$  that have been associated with O-vacancy ordering, leading to a superstructure relative to a single fluorite

(Fig. 1a and b). This finding is further confirmed by the HRTEM images in the same zone axis (Fig 1c and d).

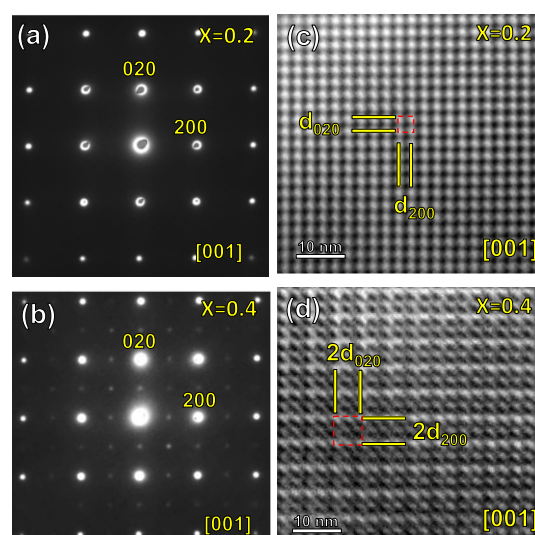


Fig. 1. HR-TEM images of La<sub>0.2</sub>Ce<sub>0.8</sub>O<sub>2-δ</sub> and La<sub>0.6</sub>Ce<sub>0.4</sub>O<sub>2-δ</sub> (a,c) with the corresponding SAED pattern (b,d) using the same calcination conditions.

Thermogravimetric and Raman analysis confirmed an increase of oxygen vacancy concentration with La-doping. The overall conductivity was determined by complex impedance spectroscopy in different atmospheres. The samples with high La-content exhibit an important proton contribution at low temperature. In addition, all samples are mixed ion-electronic conductors in hydrogen containing atmosphere.

## References

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