Chemical Imaging at Atomic Resolution as a unique tool to Refine the Structure of Individual Nanocrystals

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The challenging problem of mapping, with atomic resolution, the chemical composition of individual nanocrystals has been addressed, using a methodology based on aberration corrected electron microscopy, core-loss electron energy-loss spectroscopy and simulations. 2D atomic resolution chemical maps of octahedral-shaped $Ce_1Zr_{1-x}O_2$ nanocrystals, which showed an enhanced redox activity at low temperature, not only provide the first direct chemical evidence of an ordered cation sublattice in nanosized (20-30 nm) crystallites but, most importantly, clearly reveal a deviation of the structure from that of the expected ideal pyrochlore, which is linked to a preferential migration of the Zr^{4+} ions to the positions of the Ce^{4+} in the ideal structure. Such local chemical composition deviation within the cation network, which occurs at the level of the unit cell, is of outmost importance with regard to the structure of the complementary oxygen sublattice. Taking into account that most applications of these oxides are related to their oxygen-handling capabilities, the relevance of this finding is clear. The detection of such subtle deviations does not only provide novel structural features hardly detectable by alternative techniques but also reveal the high potential of this unique experimental approach as a tool to unveil ultimate details which maybe key to establish sounded structure-function correlations in the field of nanomaterials.

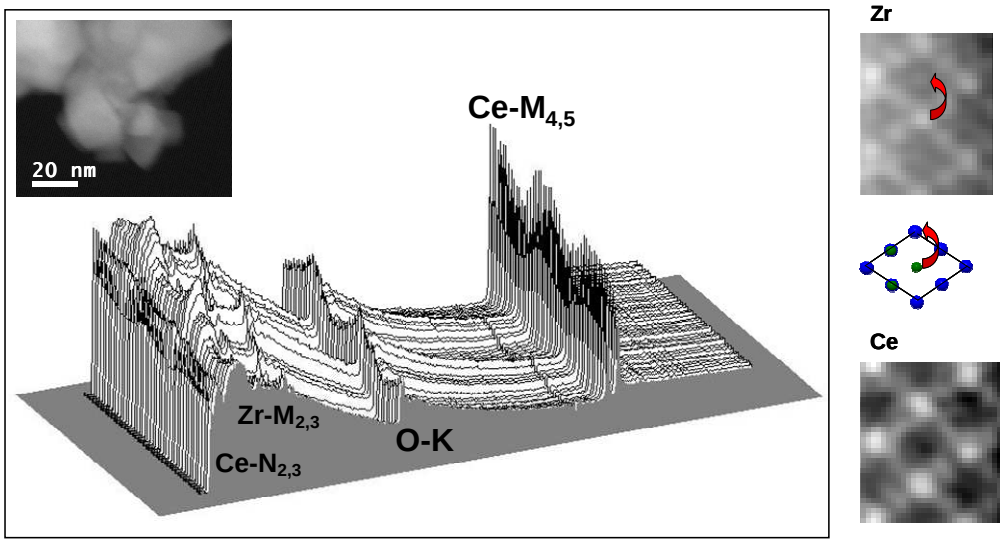

Figure.- a) 3D plot of the EELS spectra extracted from the spectrum imaging acquired on a $Ce_1Zr_{1-x}O_2$ nanocrystal. The inset image displays the HAADF image of the analysed sample b) Ce and Zr atomic resolved chemical maps of an individual nanocrystal.