Nanoscale Ordering in Oxygen Deficient Quintuple Perovskite $Sm_{2-\varepsilon}Ba_{3+\varepsilon}Fe_5O_{15-\delta}$ revealed by advanced TEM.

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The investigation of the system Ln-Ba-Fe-O (Ln=Sm, Eu, Nd, Y) in air has allowed an oxygen deficient perovskite $Ln_{2-\varepsilon}Ba_{3+\varepsilon}Fe_5O_{15-\delta}$ to be synthesized. In contrast to the XRPD pattern which gives a cubic symmetry (a_p= *3.934A*) , the combined HRTEM/ED/STEM-HAADF/EELS study shows that this phase is nanoscale ordered. The electron diffraction (ED) patterns of this phase (Fig.1a) show that whatever the crystallographic direction, [001], [010] or [100] a single a_p parameter in most of the cases cannot be observed, but instead superstructure spots, corresponding to an "$a_p \times a_p \times 5a_p$" tetragonal cell are always identified.

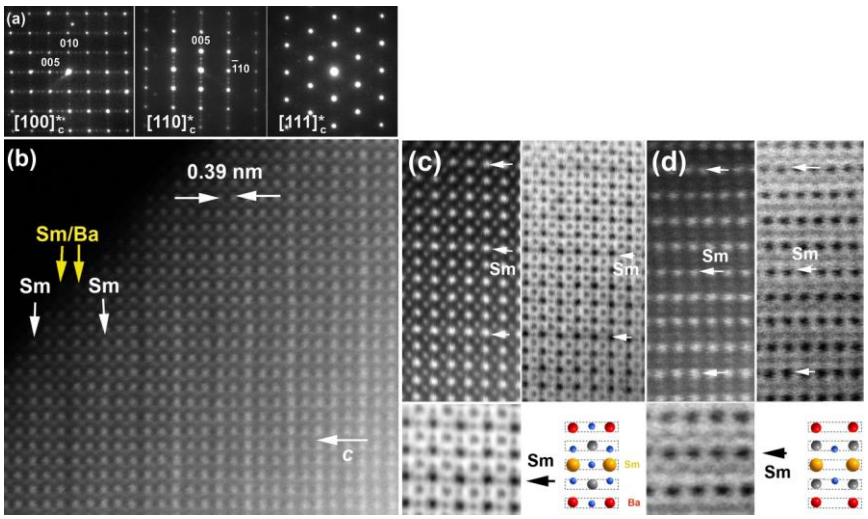

Figure 1. (a) ED patterns of the $Sm_{2-\varepsilon}Ba_{3+\varepsilon}Fe_5O_{15-\delta}$ structure. (b) HAADF-STEM image along the [100] zone axis orientation, showing a 5 perovskite unit cell contrast periodicity along the c-axis. (b) Line intensity profile over the c-direction of the HAADF-STEM image in (a); the intensity of the peaks indicates a Sm-Ba-Ba/Sm-Ba/Sm-Ba-Sm ordering; (c-d) HAADF-STEM and simultaneously acquired ABF-STEM images along the (c) [100] and (d) [110] zone axis orientation. Enlargement image and corresponding structural model is given as insert.

The HAADF-STEM image demonstrates periodic stacking sequence of the A cationic layers along the *c* axis: "Sm-Ba-Sm/Ba-Sm/Ba-Ba-Sm". It is this ordering which dictates the quintupling of the perovskite structure along one direction. Importantly, the presence of a dark line between two successive mixed Sm/Ba layers can be observed. It also appears from the measurement of inter-planar distances that the "Sm/Ba-Sm/Ba" interval between two mixed layers is larger than the other interlayer distances ("Sm-Ba" or "Ba-Sm/Ba"). Such contrast and distance variations can be attributed to the presence of oxygen vacancies and were observed in similar oxygen deficient perovskites.The oxygen lattice is imaged using atomic resolution ABF imaging in Figure 1c,d. It appears from the images along [100] and [110] orientations of a single $Sm_{2-\varepsilon}Ba_{3+\varepsilon}Fe_5O_{15-\delta}$ domain, that the oxygen positions in all the layers are close to the ideal octahedral positions except the oxygen columns in the equatorial positions close to the Sm layer. Those oxygens deviate from their ideal octahedral position, and lie closer to the Sm^{3+} cations yielding a "zigzag" contrast along [100] and [110]. No vacant oxygen sites are visible from the ABF imaging to be expected in the case of randomly distributed oxygen vacancies.

The chemical ordering is clearly confirmed by EELS mapping (Fig.2), which demonstrates that the Sm layers, spaced by $5a_p$ along the *c* axis, are practically pure and that the surrounding Ba layers are in fact not totally Sm free, but intermixed with a small amount of Sm.

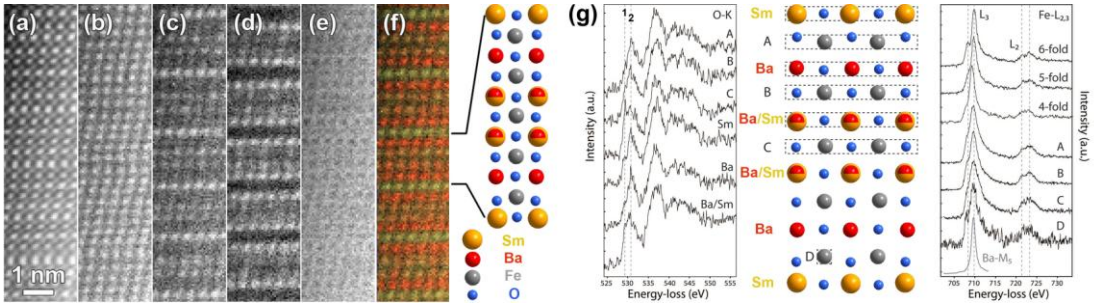

Figure 2. EELS elemental mapping of $Sm_{2-\varepsilon}Ba_{3+\varepsilon}Fe_5O_{15-\delta}$: (a) HAADF-STEM image (b) Fe-$L_{2,3}$ map (c) Sm-$M_{4,5}$ map (d) Ba-$M_{4,5}$ map (e) O-K map (f) Color overlay with Sm in yellow , Ba in red, Fe in grey and O in blue (g)EELS fine structure; (Left panel) O-K edge fine structure signatures from the regions indicated in the central panel. Structural model with indicated EELS integration areas. (Right panel) Fe-$L_{2,3}$ fine structure signatures from the regions indicated in the central panel with references for 4, 5 and 6-fold coordinated Fe^{3+}, and a simultaneously acquired and energy-shifted Ba M_5 edge.

To further investigate the presence of oxygen vacancies in the structure (which were not visible in ABF-STEM imaging due to the projected nature of the image), we used spatially resolved electron energy-loss at high energy resolution. These spatially resolved EELS data show that the O-K edge spectra corresponding to the "FeO_2" planes (labeled *a*,*b*,*c*) exhibit different intensity ratios of the two pre-peaks to the O-K edge, prepeak1/ prepeak2 at approximately 529/531 eV, depending on the nature of the surrounding "Sm,Ba" layers (Fig.2g).

All the acquired Fe L_3 edges are significantly broadened with respect to the plotted references for 6-fold, 5-fold and 4-fold coordinated Fe^{3+}. This broadening can be explained by a change in coordination of the Fe atoms within the probed atomic columns (along the beam-direction). Bearing in mind that the measured oxygen stoichiometry is 14.25, instead of 15, this suggests that the iron coordination is mainly 6, i.e. octahedral, but may also be mixed with the presence of some FeO_5 pyramids in those layers.

In conclusion, the nanodomains exhibit a unique stacking sequence of the A-site cationic layers, namely « Ln-Ba-Ln/Ba-Ln/Ba-Ba-Ln», and are chemically twinned in the three crystallographic directions. The nanoscale ordering of this perovskite explains its peculiar magnetic properties on the basis of antiferromagnetic interaction with spin blockade at the boundary between nanodomains. The variation of electrical conductivity and oxygen content of this oxide versus temperature suggest potential SOFC application. La taille de ce résumé peut faire jusqu'à 2 pages et comporter jusqu'à 4 figures avec des marges standard (2,4cm haut/bas et 2,5cm gauche/droite) sera adressé au format Word avec une police Times New Roman 10 pour tout le corps du texte qui sera justifié avec une simple interligne.

REFERENCES

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