

The structural evolution upon Y-doping from ceria (fluorite, F), to Y_2O_3 (C-type) was proved to be accompanied by the formation of complex defect structures over different length scales [1].

On the atomic scale, the dopants retain their local environment as in their pure oxide. These aggregates, defined as droplets, average into C-type nanodomains on a larger scale. By increasing the doping amount, the nanodomains are first uncorrelated, then they merge to percolate throughout the crystallite transforming the long range structure from fluorite into C-type. A side effect of this process is the formation of antiphase boundaries domains, as a consequence of the mismatch in the contact of the growing nanodomains.

Whereas C-type nanodomains are observed through PDF refinements by monitoring the vanishing of the $x(M2)$ parameter, the formation of antiphase boundaries affects the broadening of superstructure peaks only, in the Q -space patterns.

The goal of the experiment was to follow the evolution of C-type nanodomains from low to high temperature combining Rietveld and Pair Distribution Function.

The operating wavelength was moved to 0.3144 Å in order to reach high enough Q_{max} , working just below the Ce-K absorption edge, thus avoiding fluorescence radiation.

PDF scans were performed by scanning the 2θ detector over the -4° to 89° range, adding more scans in the high Q range in order to improve the signal to noise ratio. About 3 hrs scans were performed at room temperature, 4 hrs instead was the counting time at $T=450^\circ C$ and $750^\circ C$.

Besides PDF investigations, we acquired Rietveld scans in order to verify the long range structural evolution from RT to $950^\circ C$.

The data analysis was performed describing the doped samples with the C-type setting, where the only structural degree of freedom of cations is the x coordinate of one metal site (M2). In this way, the equilibrium between fluorite and C-type phases can be described by the evolution of the x coordinate of the M2 site: when it equals zero, the structure is fluorite; when it is \neq than zero, then the structure becomes C-type. This structural change is also reflected by the presence of superstructure peaks, only in the case of C-type structured samples.

Figure 1 (*left*) and (*right*) show the temperature evolution of the superstructure peaks for the sample with $\mu = 0.31$ and 0.34 , respectively. Superstructure peaks disappear for $\mu = 0.31$ and their intensity for $\mu = 0.34$ falls-off, without leading to the disappearance of the peak.

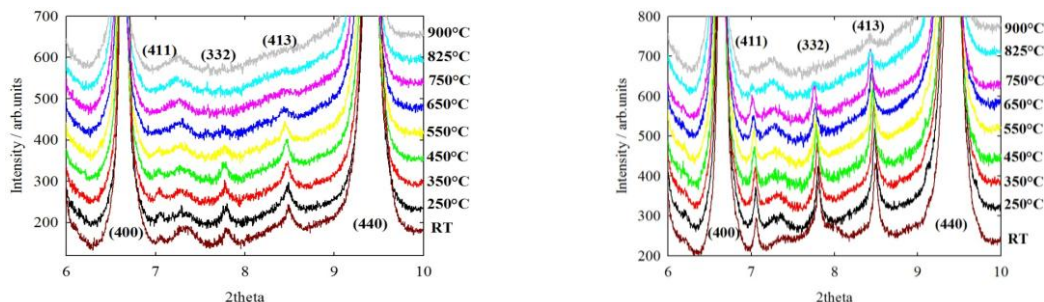


Figure 1. XRPD evolution as a function of temperature of main superstructure peaks for samples (*left*) $\mu=0.31$ and (*right*) $\mu=0.34$.

This is not just a consequence of Debye Waller. Figure 2 (*left*) shows the change of the integrated peak intensity of the (413) superstructure reflection, normalized against the (222) peak. From $\sim 400^\circ C$ on, the relative peak intensity decreases with temperature. The results of Rietveld refinements are reported in Fig 2 (*right*), where the temperature evolution of the $x(M2)$ is shown. The change in relative intensity of superstructure peaks corresponds to the vanishing of $x(M2)$.

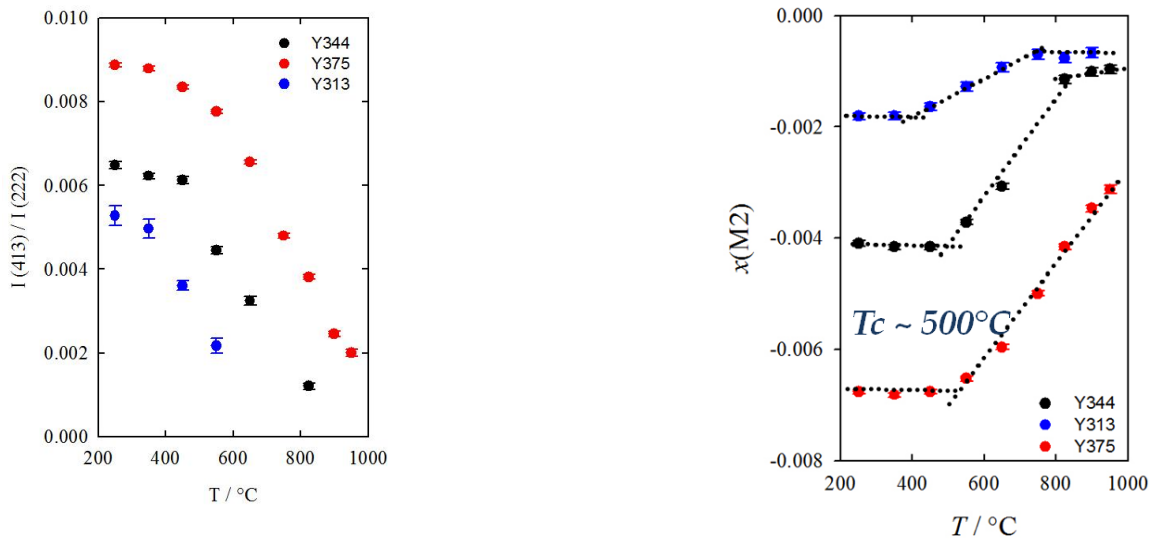


Figure 2. Temperature evolution of (left) relative intensity of main superstructure peak and (right) x coordinate of the M2 site as found by Rietveld refinements. Blue: $\mu=0.31$, black: $\mu=0.34$, red: $\mu=0.38$.

The high resolution patterns showed the tendency of C-type samples to transform into fluorite while increasing temperature. As a consequence of the intensity decrease, it is hard to monitor the peak broadening evolution as a function of temperature. Nevertheless, insights into the nanoscale structure evolution with temperature can be gained through the Pair Distribution Function. In this respect, the samples with $\mu = 0.34$ and 0.38 show no noteworthy changes compared to low temperature, that is with nanodomains in the order of 15 nm. Conversely, the sample with $\mu = 0.31$, which showed ~ 10 nm size domains at low temperature, revealed no C-type nanodomains at high temperature. Since the cationic substructure is expected to mirror the oxygen vacancies distribution, these results suggest that up to $\mu \sim 0.31$ at high temperature the oxygen vacancies are more randomly distributed compared to low temperature and to heavier doped samples.

References:

1. M. Coduri, M Scavini, M Allieta, M Brunelli and C Ferrero, "Defect structure of Y-doped ceria on different length scales" *Chemistry of Materials*, 2013, **25**, 4278-4289.