In-situ Growth of epsilon-Fe2O3 Nanoparticles Embedded in SiO2 Sol-gel Films by XAS – Experiment MA-3199

XAFS study of the phase development in epsilon with temperature treatment

EXAFS spectra of the powders obtained at different annealing temperatures are shown in figure 1. A first change is observed for the spectrum of the mild annealing (300k) respect to the untreated sample as can be originated by a structural change. EXAFS signal evolves slightly in the range 300 to 600K, but upon this temperature, signs of other contribution to the oscillatory signal appear. These changes are more clearly detected in the range 900 to 1100, where additional contributions modulate the signal. In the final condition, at 1200K, the oscillatory spectrum is largely different to the formers and can be indicative of the formation of a new phase.

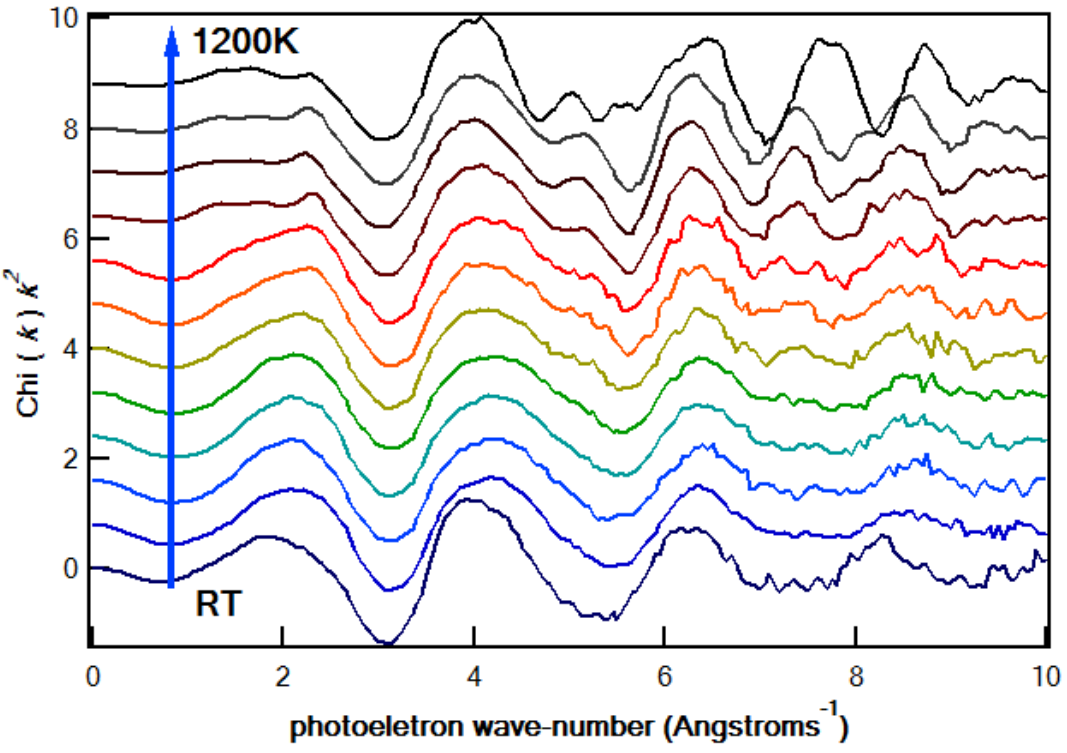

Figure 1. EXAFS spectra of the powder samples annealed at different temperatures versus the photoelectron wave-number.

The Fourier analysis of the oscillatory EXAFS signal provide local structure information in the real space. In figure 2 the Fourier transform of the EXAFS spectra are presented. In this case, differences in the local structure are more intuitively detected. The intensity of the first peak (and the absence of a clear second peak) in the RT sample suggest certain lack of crystallinity. The first peak is associated to the first atomic coordination shell of the Fe, which in case of oxides is an oxygen shell. However, another factors can affect this intensity, like a different environment (different speciation) or a larger static disorder. In case of the first condition, some amount of N can be present from the precursors. Throughout the annealing, main changes are observed first in the development structure, as arises from the increase of intensity in the second feature of the spectra at about 3A. The intensity increase is a effect of the improvement of the cristalinity, which reaches its maximum for the epsilon phase at about 900K. Respect this condition, when the temperature is increased by only few degrees, upon 960K, the relative peak intensity tendency of the two main contributions clearly changes, becoming the second contribution more prominent than the first one. Upon the annealing to higher temperatures the structure seems to keep stable until the temperature exceed 1200K, for which an abrupt structural change is observed.

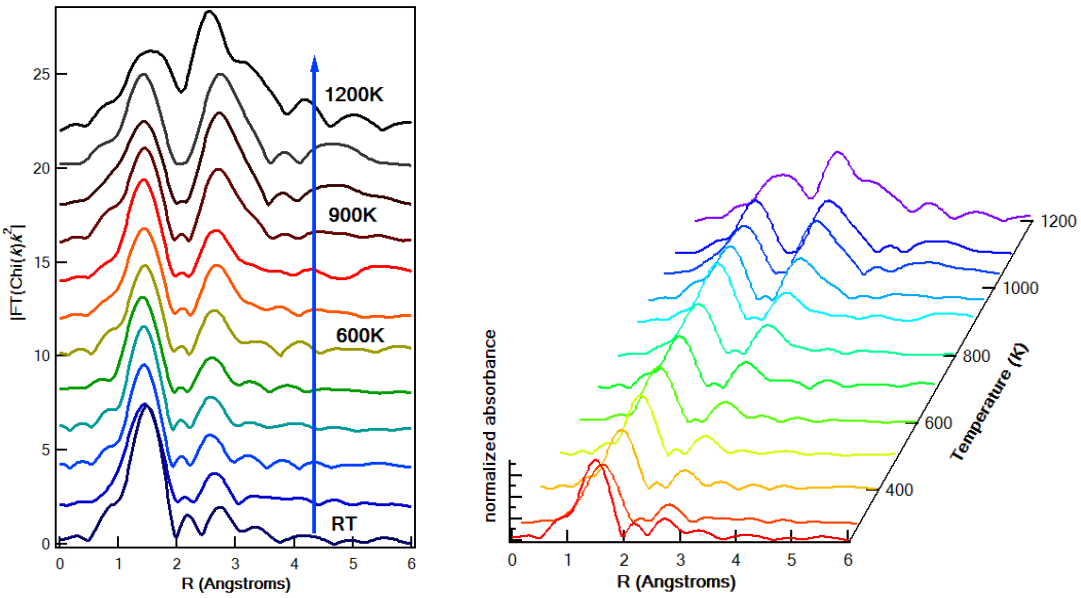

Figure2. Fourier Transform of the EXAFS spectra of the epsilon powder samples obtained at different temperatures.

The results of the XANES spectra clarify the chemical evolution along the annealing. In figure 3, the XANES of the same set of conditions is presented. Three main features of the spectra have been examined, namely (i) presence and shape of pre-peak, (ii) shape and intensity of the main peak of the edge and (iii) additional features/ resonances after the main peak. The presence of pre-peak is a common feature in most of Fe oxides and Fe compounds []. However, it usually appears associated to structures with symmetries in which an inversion center exists []. The position, shape and height of the pre-peak can give information about the local geometry of the Fe atoms. Still, in case of the not annealed condition, the pre peak shows a slightly different shape respect to the other conditions. The pre-peak is present in almost all the conditions but in the 1200K annealed sample, it shape completely changes, suggesting a major chemical change.

Regarding the main peak, the temperature-dependent evolution can be easily followed. More interestingly, at 600K the particular shape of the epsilon spectrum [] is observed.

Upon to higher annealing temperatures, the main peak sharpens and slightly moves to lower energy, showing typical features of alpha phase, but also in case of the 1200K condition, a broadening of the main peak. The transition to alpha phase for temperatures higher than 600K can also be followed by the appearance of a second resonance after the main peak, which is completely developed at 1100K. Finally, at 1200K, the largest list of changes are observed, including to the aforementioned, oscillations in the low k region (end of the XANES zone).

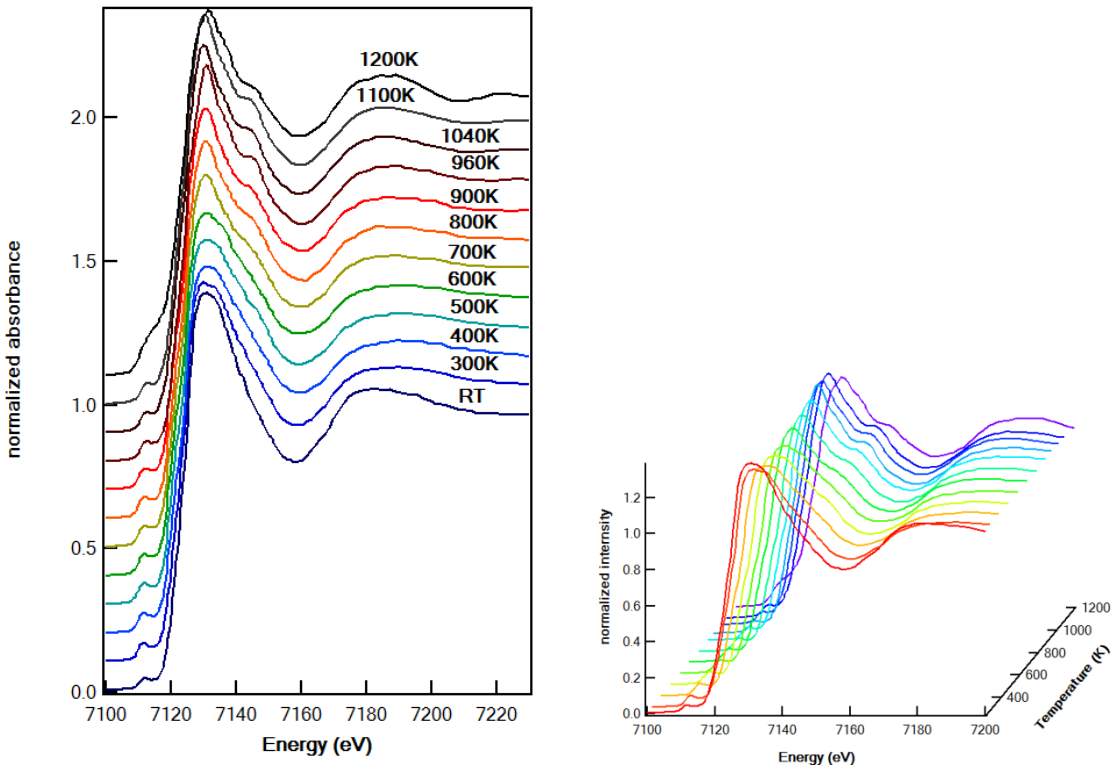

Figure 3. XANES of the annealed epsilon powder samples.