Report MA-2164

"XANES and EXAFS characterization of epsilon-Fe2O3 nanoparticles in SiO2 sol-gel thin films for magnetic and electronic applications"

The DW factor (a parameter that accounts the correlated factor of order/disorder between the atoms in the lattice by means of the correlated dispersion in the mean distances) has been set to have the same value for the equivalent type of pairs of atoms (i.e. for Fe-O pairs, Fe-Fe pairs, etc).

In order to take in account the possibility of the existence of O surface vacancies in the lattice by nanometer size effect, we have left an additional degree of freedom in the number of O neighbors in both shells: each shell can display a different mean number of neighbors, but this in the first shell should be larger or equal to it in the second shell.

Results.

In fig. 1 the EXAFS spectra of the references and samples are presented. There are clear differences in the k space at short k values between the samples and the reference oxides, pointing out the presence of a different Fe phase in the samples out of the current oxides. At intermediate k values the similarities are more than the differences for most of the samples. There is a mention apart for the rm960-1, which oscillation pattern is clearly differentiated from any of the present spectra. For a detailed analysis of the oscillation spectra, a fit to a multiple-shell model is performed in both k and R space, which is obtained by the Fourier transform analysis of the k-space weighted in k^3.
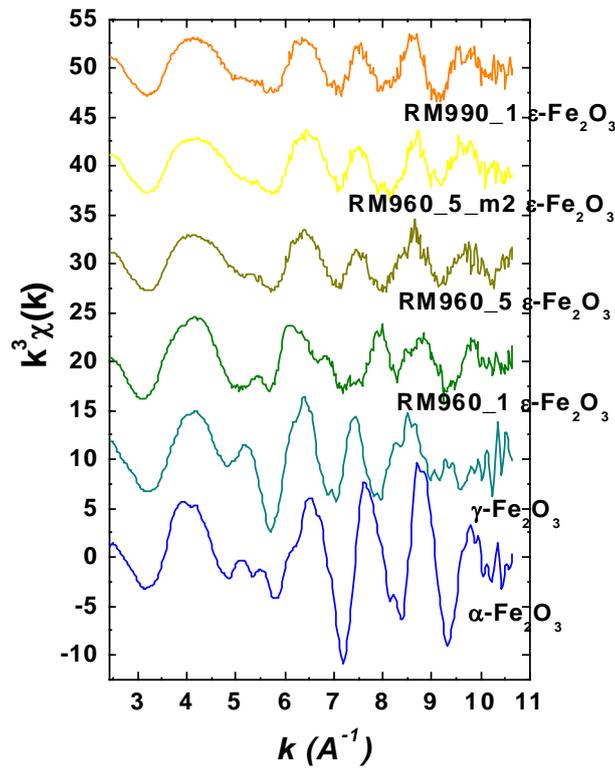
Figure 1. EXAFS spectra of the references and samples in the *k* space.

The R-space representation of the spectra gives a set of spectra displayed in the real space (fig. 2). These spectra should be interpreted as the sum of the multiple scattering paths experimented by the electron in the short-range atomic surrounding within the lattice around the atom of origin (Fe). In this representation we see the scattering amplitude in function of the distance from the original atom. The amplitude displayed in this figure is proportional to the scattering probability. In a simplified case we can say that each peak correspond to an average atomic neighboring shell.

In order to fit these spectra we will assume a simple model in which only the first mean neighbor is considered. The EXAFS fits of this first neighbor have demonstrated that the fit with a model that supposes a single O shell, like characteristic of a gamma-Fe2O3 structure, does not adjust in a proper way. Thus, in this case we can completely

discard the gamma-Fe2O3 structure to be the representative of the samples. It should be commented that the fits to a gamna-Fe2O3 single shell has yield to correlation coefficients larger than 25, at least 5 times larger than the obtained by the epsilon or alpha two shell models. This fact leads us to affirm that the local structure of the samples is closer to the local structure corresponding to alpha or epsilon phases.

The applied model implies a double O shell that uses an Epsilon-Fe2O3 and a alpha-Fe2O3 references to obtain a multiple-path file to perform the fits. We have applied both models to all the references in order to obtain the better fit in the simplest and most physically consistent way. For this purpose, the epsilon reference, dueto the multiple O shells has been simplified to be a double O-shell meanwhile the alpha reference has been full applied within the studied range of R.

As can be observed in the Table 1, the epsilon model offers a poorer fitting respect the alpha model. Nevertheless it should be noted that both models give very similar fitting results. In this sense, the alpha model has given a better fit in all the analyzed samples. The difference in the fitting correlation can be due to as the alpha paths are calculated from a double shell reference it works better for a case in which there are not needed additional shells. In the successive analysis of the EXAFS we will take the results obtained with the shells taken from the FEFF paths obtained from the alpha reference.

The fitting results for the models are summarized in Fig.2. In this space, there are clear differences between the samples and the references. Regarding the spectra of the samples, the most significant difference is noticed between the rm960 and the other synthesized samples, more pronounced for the second neighbor.
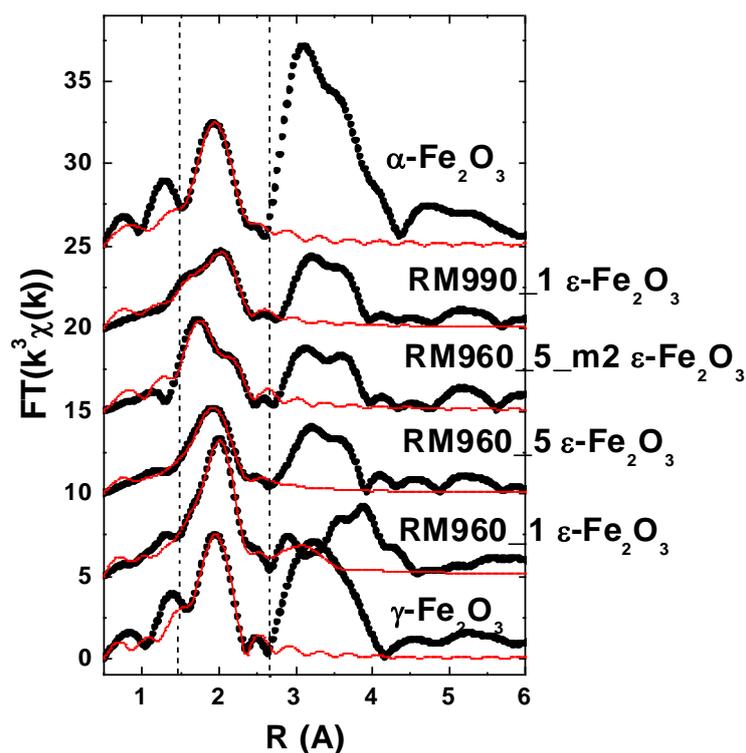
Figure 2. EXAFS spectra in the R space representation obtained from the Fourier Transform of the spectra in the wavenumber space, with the corresponding fits obtained for the R range from 1 to 2.6 A.

The results of the fittings for the first neighbor are summarized in the tables 1 and 2. At table 1, the fitting parameters obtained for the fitting by the paths obtained from the epsilon reference are presented. In table 2, the paremeters correspond to the fitting with the paths calculated from the alpha reference. As we commented above, we will take the second results for the discussion, although we will present both.

**Table 1. fitting parameters obtained with the Epsilon paths model**

Sample	shell	R (A)	N	DW	Corr R (%)
α- Fe$_2$O$_3$	Fe-O	1.9027	6.17526	0.004936	5.3166
	Fe-O	2.0578	4.9968		
γ-Fe$_2$O$_3$	Fe-O	1.9564	10.0755	0.001720	5.9134
RM960-1	Fe-O	1.8851	6.2965	0.000685	8.121
	Fe-O	1.9982	6.6253		
RM960-5	Fe-O	1.8300	3.8925	0.002265	5.096
	Fe-O	1.9699	4.4228		
RM960-5m2	Fe-O	1.7686	5.4427	0.001160	9.649
	Fe-O	1.9455	5.4179		
RM990-1	Fe-O	1.7923	3.1737	0.002582	5.270
	Fe-O	1.9641	7.7873		

Table 2. EXAFS fitting parameters obtained with theAlpha paths model

sample	shell	R (A)	N	DW	Corr R (%)
α- Fe$_2$O$_3$	Fe-O	1.9049	5.5498	0.006451	4.06 0
	Fe-O	2.0610	4.8677		
RM960-1	Fe-O	1.9499	6.5716	0.006082	4.724
	Fe-O	2.0741	5.1550		

RM960-5	Fe-O	**1.8403**	**3.9276**	0.002148	4.569
	Fe-O	**1.9814**	**4.5144**		
RM960-5m2	Fe-O	**1.7764**	**5.3084**	**0.001816**	5.291
	Fe-O	**1.9540**	**5.3602**		
RM990-1	Fe-O	**1.8060**	**3.1038**	**0.003027**	3.266
	Fe-O	**1.9752**	**8.0836**		
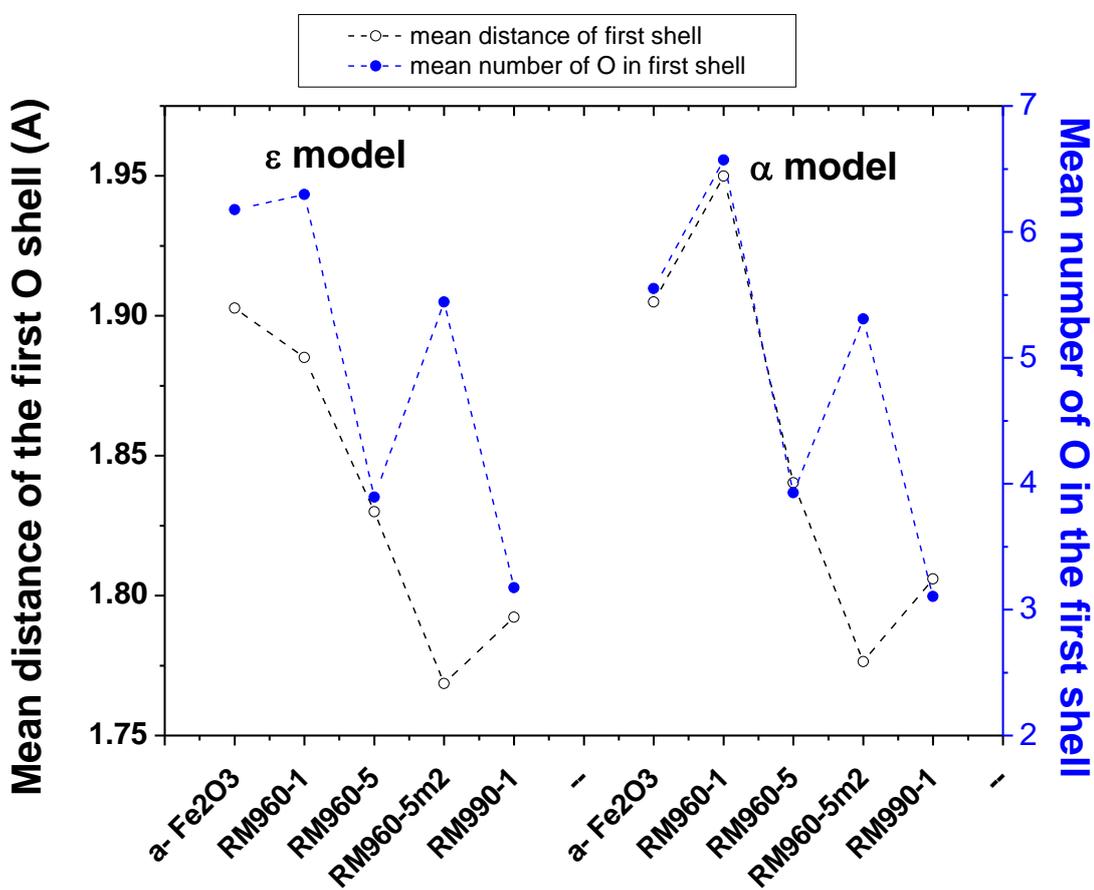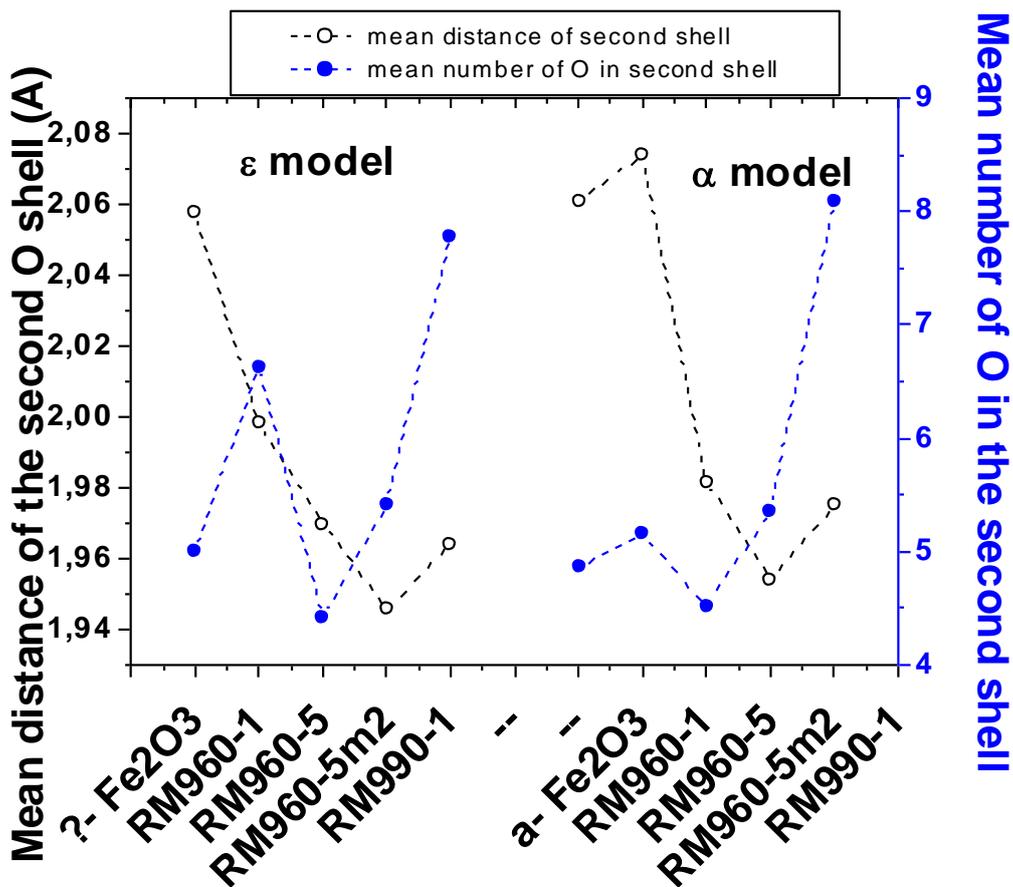
As discussed previously, the Debye-Waller factor gives account of the correlated atomic disorder of the lattice. We can compare the relative order in the Fe-O (short term order) shell by comparing this parameter within the studied samples. From the results shown in fig.3., we can observe that in the epsilon model, the samples posses a higher order than the alpha reference, keeping in a range of 0.0006-0.0022. Thus, it can be supposed at a glance that the synthesis process gives a good crystallinity at least at short range, higher than the observed for the reference. In case of the alpha model, we obtain higher DW values than for the epsilon model that implies lower order. In addition, the order parameter is more homogeneous except in case of the rm960, which is closer to corresponding to the alpha reference.
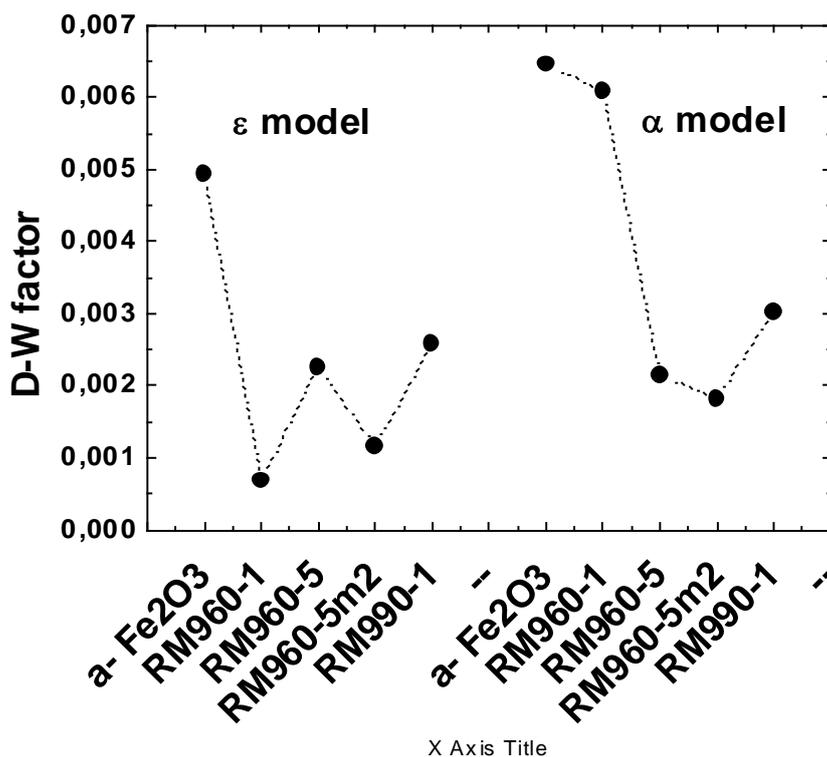
Fig.3. Debye Waller factor obtained from the EXAFS fit of the first neighbor of the samples and alpha reference in the R space from a path model calculated from an epsilon and from an alpha reference.

Finally, we can consider further neighbors in the R space to make a qualitative analysis. First, we observe clear differences between the rm960-1 and the other samples, which present evident similarities. The rm960-5/5-m2 and rm990 present a second peak in the proximities of 3.3 A, all of them with a very similar shape. This distance is close than the position of the second neighbor of alpha and gamma. Discarding the presence of gamma from the EXAFS analysis, we can attribute this peak to the existence of a undetermined amount of alpha phase within the structure of the mentioned samples. In the same way, this fact can lead us to suppose the absence of alpha phase in the rm960-1 sample.