Supplementary Information to:

Structural determination of Bi-doped magnetite multifunctional nanoparticles for contrast imaging.

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1. Fe K-edge XAS Characterization

Fig. 1 compares the Fe K-edge XANES spectra recorded on PAM7 to a group of typical Fe oxide and hydroxide references. The formation of any of this references (instead of magnetite/maghemite) can be discarded since the spectral profile of these references is clearly different from that of PAM7. In the same way, the simultaneous formation of several of these phases can be discarded since any mixture of these phases would result in a poorly shaped profile that does not match the PAM profile to a good degree of satisfaction (for an illustrative example see inset in Fig. 1).



Fig. 1 Comparison of the Fe K-edge XANES spectra recorded on the representative PAM7 sample and a series of reference samples. In the inset the PAM7 spectra is compared to the best fit obtained by combining goethite (67%), hematite (21%) and FeO (12%).

The Fe K-edge EXAFS spectra of the Bi-doped iron oxide nanoparticles, shown in Fig. 2, indicate that the crystal structure is the same as in bulk maghemite and magnetite references. In addition, the structural environment of the Fe atoms remains unaltered and highly ordered for all the samples.

To study how the local distortion caused by Bi substitution can affect the Fe K-edge EXAFS spectrum (i.e. the local environment around Fe) several distortion models have been simulated modifying the interatomic distances relative to the initial values in Fe_3O_4 and keeping them fixed. For the simulation shown in the main text we have assumed that when a Bi atom substitutes Fe in the spinel lattice its environment get distorted in such a way that the Bi-O distance increases moving the O atoms far from the Bi and 0.15 Å closer to the absorbing Fe. The Fe-Bi distance also increases 0.25 Å. Other probed models for the local



Fig. 2 Experimental Fe K-edge EXAFS spectra of bismuth-doped iron oxide nanoparticles and reference samples.

distortion are: (a) no structural distortions are caused around the absorbing Fe, (b) the O atoms between the central (absorbing) Fe and the substituting Bi are pushed 0.25 Å closer to the absorbing Fe, the Fe-Bi distance increases 0.40 Å respect to the initial Fe-Fe distance and the oxygen atoms at a distance larger than the initial Fe-Fe distance also move 0.40 Å away from Fe, (c) all the lattice expands by an isotropic expansion coefficient: $0.125 \times$ undistorted distance. The rest of the fitting parameters have been kept fixed as well: amplitude=0.76, change in Fermi Energy $\Delta E=0$ and Debye-Waller factors $\sigma^2 = 0.006$ Å² and 0.009 Å² for the first coordination shell and for the further atoms, respectively. For the FT a k-range from 2.5 Å⁻¹ to 12 Å⁻¹ has been chosen. In all the cases a Hanning window has been used for filtering and no phase correction has been applied. The corresponding simulated EXAFS are illustrated in Fig. 3. In all the cases gradual modifications of the Fourier transforms are observed, in contrast to the experimental results.

In order to compare to the experimental results, the simulations in Fig. 3 show the average response of all the Fe atoms. Fig. 4 shows how the Fe-O and Fe-Fe scattering paths change when Fe is substituted by Bi in the (b) model i.e. the modification corresponding to a single Fe atom that has a Bi atom nearby.



Fig. 3 FEFF calculated modulus of the Fourier transform of the Fe K-edge EXAFS spectra for 0, 2 and 7% substitutional Bi in the Fe_3O_4 crystal structure: (a) the distances between atoms have been kept those of the manganite, (b) the O atoms between the central (absorbing) Fe and the Bi are pushed 0.25 Å closer to the absorbing Fe, the Fe-Bi distance has been increased 0.40 Å and the oxygen atoms at a distance larger than d(Bi-Fe) have been also moved 0.40 Å away from Fe, (c) all the lattice expands isotropically: the Fe-O distances, consequently, increase ~ 0.25 Å and Fe-Bi ~ 0.40 Å.



Fig. 4 Contribution of the Fe-O (top) and Bi(Fe)-Fe (bottom) scattering paths to the FT [Modulus (black) and real part (red)] of the Fe K-edge EXAFS in the cases of the initial magnetite structure and that distorted according to model (b). The inset shows an schematic view of the geometry of the paths

2. Bi L₃-edge XAS Characterization

In the comparison in Fig. 5, it can be seen that the absorption spectrum of the representative LP10 sample strongly deviates from that of Bi metal, $BiFeO_3$ and the precursors, the spectral profile of LP10 being simpler. The reference spectra, on the other hand, have a rich profile, indicating well crystalized structures. The comparison in Fig. 5 indicates that the amount of Bi atoms still in the precursor form, if any, should be small. The close resemblance between the XANES profiles of LP and PAM samples, synthesized using different precursors, also discards a noticeable amount of precursor in the final product.

One might initially suggest a mixture of α -Bi₂O₃ and β -Bi₂O₃ to account for the XANES profile of the LP and PAM nanoparticles. However, a linear combination analysis shows that the XANES profile of our nanoparticles cannot be satisfactorily explained with the presence of mixed polymorphs (see Fig. 6). A combination of α - and β -Bi₂O₃ cannot match the shoulder-like structure below the edge (A1, ~ 13428 eV). At this point it is worth to recall that a reference foil was measured simultaneously to all the spectra. Therefore, the difference in feature A1 cannot be associated to energy miscalibration. The region above the edge also shows significant differences with the experimental profile. Including the precursor in the linear combination fitting does not lead to a significant improvement of the fit: the fit is better for the edge region, but it gets worse above the edge.



Fig. 5 (a) Comparison of the experimental Bi L_3 -edge XANES spectra of the representative LP10 sample and a series of reference samples: Bi (acet)₂, Bi (NO₃)₃, Bi metal and BiFeO₃. A simple fingerprint analysis discards the presence of Bi-containing precursors, as well as BiFeO₃ and metallic Bi.(b) Comparison of the experimental Bi L_3 -edge EXAFS spectra of the LP10 and TD03 samples and a series of reference samples: Bi (acet)₂, Bi(NO₃)₃, Bi metal and BiFeO₃.



Fig. 6 (a) Comparison of the experimental Bi L₃-edge XANES spectra of the representative PAM sample and the best fit obtained for a linear combination of α -Bi₂O₃ and β -Bi₂O₃. The best fit relative contents are: α -Bi₂O₃ 50% and β -Bi₂O₃ 50% (b) Same comparison including the Bi precursor in the fitting. The best fit relative contents are 64% α -Bi₂O₃, 12% β -Bi₂O₃ and 24% Bi(NO₃)₃.

Computational XANES details

The ab-initio computation of the XANES spectra was carried out using the multiple-scattering code Continuum included in the MXAN package. For the computations the potential for the different atomic clusters was approximated by a set of spherically averaged muffin-tin (MT) potentials built by following the standard Mattheis' prescription. The muffin-tin radii were determined following the Norman's criterion.

To compare the XANES experimental spectra to the results of *ab-initio* Bi L_3 -edge computations, we need first to find the more appropriate choice of several computational parameters by using well known

reference compounds^{1,2}. Thus, initially we have computed the theoretical spectrum for metallic Bi and $BiFeO_3$.



Fig. 7 Comparison between the experimental Bi L_3 -edge XANES of metallic Bi (blue, \circ) and BiFeO₃ (black, \bullet) and the computations performed by using the DH ECP and ovf = 1%.

For the reference compounds we have first determined the minimum size of the cluster needed to reproduce all the features of the experimental XANES spectrum. This is made by adding progressively coordination shells surrounding the absorbing atom until convergence is obtained, i.e. the addition of further shells do not lead to the modification of the relative energy separation and intensity of the spectral features or to the appearance of new ones. The final computation of the theoretical XANES spectrum of metallic Bi has been made on a cluster of 75 atoms covering all the scattering contributions within the first 8 Å around absorber Bi³. In the case of BiFeO₃ the cluster contains 82 atoms covering all the interatomic distances within a 6 Å radius around central Bi⁴. In a second step we have checked the influence of the overlapping factor (ovf) used to build up the scattering potential into the reproduction of the experimental XANES spectra and the effect of modifying the value of the maximum angular momentum quantum number, l_{max} , needed to account for the experimental absorption spectrum in the first ~ 50 eVs. Last but not least we have studied the best choice of the exchange and correlation part of the final state potential (ECP) to reproduce not only the spectral shape but also the intensity of the computed spectral features and their relative energy separation. To this end we have performed the computations by using (i) the energy dependent Hedin-Lundqvist (HL) ECP potential, (ii) the energy dependent Dirac-Hara (DH) ECP potential, (iii) only the real part of the HL ECP (hereafter real HL) and (iv) by adding the imaginary part of the HL ECP to the Dirac-Hara one (hereafter complex Dirac-Hara). The best reproduction of the experimental XANES spectra was obtained by using the Dirac-Hara ECP potential and by imposing a 1% of overlapping factor, in agreement to previous works for transition metal oxides and related compounds^{5–7}. The results of the computations are reported in Fig. 7. It should be noted that the energy scale of each computation is referred to its own muffin-tin potential. Therefore, it is necessary to correct the energy scale of the computed spectra in order to compare the calculations for the different compounds in a unique energy scale and monitor the edge-shift associated to the different structural arrangement around Bi, i.e. to the modification of the interatomic distances^{2,8}. The excellent agreement obtained allows us to fix several computational parameters: hereafter all the calculations have been performed by using a 1% overlapping factor and the DH ECP potential. In addition, in all the cases, the theoretical spectra have been convoluted with a Lorentzian shape function (Γ = 1.5 eV for Fe K edge, 5.98 eV for Bi L_3 edge) to account for the core-hole lifetime⁹ and the experimental resolution. The theoretically calculated spectra have been directly compared to the experimental XANES spectrum i.e., no fitting procedure (free parameter) has been used during the calculations. The assessment of the quality of the theoretical computations is based on the correct reproduction of the shape and energy position of the different spectral features and of their relative energy separation and the intensity ratio.



Fig. 8 (a) Comparison between the experimental Bi L_3 -edge XANES of α -Bi₂O₃ (red, \circ) and the theoretical calculations performed by using the complex DH ECP and by progressively increasing the cluster size (see text for details). In order to get an enhanced view of the differences the result of the computations obtained by using the real DH are also shown. (b) Same as above, using only the real DH computations, in the case of β -Bi₂O₃ (black, \bullet).

Next, we have computed the XANES spectra for α -Bi₂O₃ and β -Bi₂O₃ polymorphs¹⁰. In the case of α -Bi₂O₃, since Bi occupies two different crystallographic (4e) positions denoted as Bi1 and Bi2¹⁰, the computation of the absorption cross section has to be performed separately for Bi absorbing atoms occupying both crystallographic sites. The XANES spectrum is obtained by adding both contributions with the weighting dictated by the crystallographic occupancy. Computations have been done for different cluster sizes: starting from the smallest Bi-O coordination polyhedron, corresponding to the photoabsorbing Bi and its first oxygen coordination shell, and adding progressively further coordination shells. The results of these calculations, shown in Fig. 8, indicate that a good reproduction of the experimental spectra requires a cluster including, at least, two coordination shells. In this way the relative energy separation of the spectral features is accounted for by the calculations, especially regarding the high energy resonances C (in α -Bi₂O₃) and D $(\beta$ -Bi₂O₃). In other words, the inclusion of Bi-Bi coordination is mandatory to account for the experimental spectra.

The computations above can now be used to confirm that the XANES spectra of the samples under study cannot be explained as a fraction of Bi atoms in the local arrangement of α -Bi₂O₃ and also a fraction of Bi atoms in a β -Bi₂O₃ fashion. If this was the case, the theoretical computations above would indicate that the local order around Bi includes not only oxygen but also the second shell, implying the existence of Bi-O-Bi coordination. However, no Bi-O-Bi coordination can be detected in the nanoparticles synthesized by laser pyrolysis or precipitation in aqueous media.

Finally, we have computed the XANES spectra by considering that Bi substitutes Fe in several iron oxides: magnetite, maghemite and hematite. We have built-up clusters in which a single Bi atom occupies the photoabsorber position and we have included all the scattering contributions from atoms within the first 7.5 Å around Bi. The scattering contributions used are those derived from the structural parameters reported in the literature: α -Fe₂O₃¹¹; γ -Fe₂O₃¹²; and Fe₃O₄¹³. In the case of γ -Fe₂O₃ and Fe₃O₄ two different crystallographic positions (8a) and (16d) may be occupied by Bi. Consequently the computation has been performed separately for each site and the XANES spectrum has been obtained by adding both contributions with the weighting dictated by the crystallographic occupancy. As it can be seen in Fig. 9, these theoretical results do not agree with the experimental spectra. This indicates that Bi does not enter in the iron oxide structure, as suggested by the results at the Fe K edge.



Fig. 9 Comparison between the experimental Bi L_3 -edge XANES of PAM7 (•) and the theoretical calculations performed by considering that Bi substitutes Fe in maghemite, hematite and magnetite.

Local environment around Bi - Second shell

To gain a deeper insight into the origin of the small feature at $R \sim 2.8-3.8$ Å in the Bi-edge FT of LP10 and PAM7 we have compared its contribution to the experimental EXAFS (i.e. the Fourier back-transform) with the contribution to the EXAFS that one could theoretically expect from a particular type of atom at a given distance. The very small feature that shows at ~ 3.2 Å cannot come from Bi neighbors since, as evidenced in Fig. 10, heavy atoms contribute to EXAFS with large amplitude oscillations up to higher k. The same conclusion is drawn for Fe. On the other hand, the simulations corresponding to a single scattering from a light atom, such as O, or a multiple O-Bi-O scattering at ~ 4 Å seem to better fit the Fourier back-transform of the experimental data. Therefore, these results further support the lack of a Bi-Bi or of Bi-Fe scattering path.



Fig. 10 Modulus and real part of the Fourier filtered (back-transformed) EXAFS oscillation (Bi L_3 edge) corresponding to the 2.8-3.8 Å range (second shell) of the LP10 and PAM7 samples. FEFF simulated Fourier back-transforms corresponding to a single scattering of a Bi atom at R= 4 Å, a single scattering of a O atom at R= 4.2 Å, and a multiple O-Bi-O scattering at R = 4 Å.

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