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Unusual distribution of the constituents of an $(Fe_2O_3)_{0.8}(SnO_2)_{0.2}$ nanocomposite evidenced by ^{57}Fe and ^{119}Sn Mössbauer spectroscopy

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A comparison of ^{57}Fe and ^{119}Sn Mössbauer spectra suggests the formation of island-type tin-containing segregations around the smallest α-Fe_2O_3 grains.

Nanosized binary oxide systems improve various characteristics of gas sensor materials.[1] In order to better understand the nanoscale organization of such materials that cannot be properly characterised by X-ray diffraction analysis, spectroscopic techniques should be used. Mössbauer spectroscopy provides information on the electronic state and local surrounding of the resonant probe atom in the test material. A binary oxide system suitable for Mössbauer characterization is α-Fe_2O_3–SnO_2. In this case, both ^{57}Fe and ^{119}Sn ‘spectroscopically easy’ nuclei can be applied. Moreover, as one of the constituents is magnetically ordered (α-Fe_2O_3 is an antiferromagnetic with T_N = 960 K), the ^{57}Fe spectra characterise the size distribution of α-Fe_2O_3 crystallites.[2] Another advantage of the system is the spin polarization of diamagnetic tin ions by neighbouring 3*d* cations. This leads to magnetic hyperfine splitting of the ^{119}Sn absorption pattern, which allows one to monitor the distribution of tin ions with respect to magnetically active α-Fe_2O_3 crystallites.[3] The ^{119}Sn hyperfine splitting parameters were reported[3–5] for samples containing small amounts of Sn^{4+} ($\leq$ 0.5 at.%) located in the bulk of crystalline α-Fe_2O_3. At 295 K, the Sn^{4+} ions were characterised by the transferred hyperfine field H(Sn) = 123 kOe and the isomer shift δ = +0.15 mm s^{-1}. These Mössbauer parameters allowed one to identify Sn^{4+} located within an α-Fe_2O_3 lattice. The upper limit of the Sn^{4+} content in the bulk of ferric oxide particles for samples obtained by co-precipitation of Fe^{3+} and Sn^{4+} hydroxides with subsequent annealing in air at 900 °C was close to 1 at.%.[3] The Sn/Fe = 1:1 composition prepared under similar conditions exhibited the superparamagnetic behaviour of α-Fe_2O_3 crystallites with a small size (d < 14 nm).[6]

The samples for Mössbauer measurements were synthesised by co-precipitation of tin and iron hydroxides from a nitric solution containing Sn^{4+} and Fe^{3+} ions in 1:200 (sample A) and 1:10 (sample B) atomic ratios with hydrazine hydrate followed by drying and annealing the hydroxides at 500 °C. The measurements were performed using a constant-acceleration device with $Ca^{119m}SnO_3$ or ^{57}Co(Rh) sources at 80 and 295 K. Isomer shift values refer to $CaSnO_3$ or α-Fe at 295 K. XRD analysis revealed the presence of a single α-Fe_2O_3 phase with the average particle size d_{XRD} = 26 or 13 nm for samples A or B, respectively.

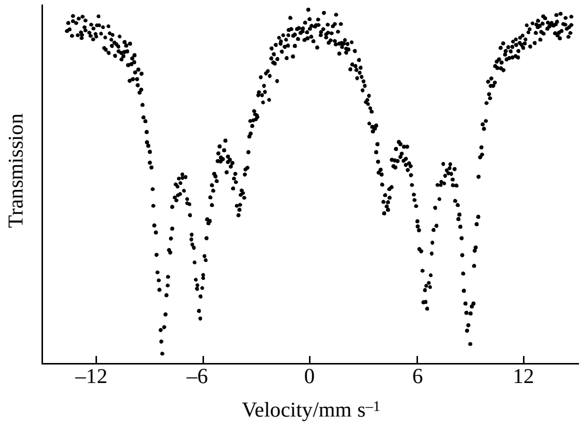

Figure 1 Mössbauer spectrum of $^{119}Sn^{4+}$ in the bulk of α-Fe_2O_3 (sample A) at 295 K.

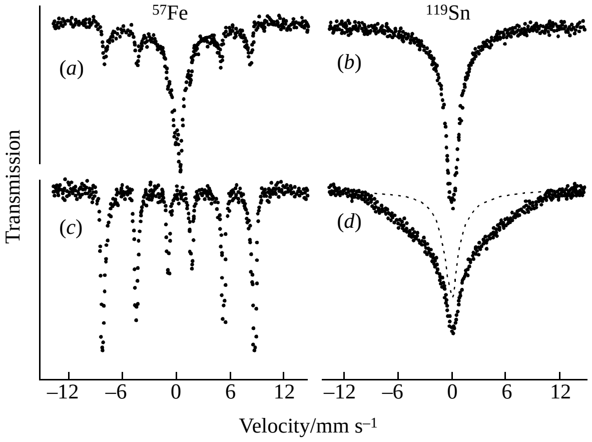

Figure 2 ^{57}Fe and ^{119}Sn Mössbauer spectra relative to the $(Fe_2O_3)_{0.8}(SnO_2)_{0.2}$ nanocomposite (sample B) at (*a*), (*b*) 295 K and (*c*), (*d*) 80 K. The dashed line represents the residual non-magnetic contribution calculated from the distribution of H(^{119}Sn) values according to Hesse and Rübartsch.[8]

The use of hydrazine hydrate as a precipitating agent was recommended for the preparation of (Fe_2O_3–SnO_2)-based sensor materials.[7] However, the tin-doped α-Fe_2O_3 samples, which were previously studied by ^{119}Sn Mössbauer spectroscopy,[3–5] were obtained using aqueous ammonia. Thus, sample A allowed us to compare the distributions of tin ions in these two cases.

^{57}Fe Mössbauer measurements confirmed the formation of crystalline α-Fe_2O_3 (the presence of a unique sextet with H = 510±5 kOe, δ = 0.38±0.04 mm s^{-1} and quadrupole shift ε_Q = = −0.10±0.03 mm s^{-1} in the room-temperature spectrum). The ^{119}Sn spectrum (Figure 1) consists of a well-resolved hyperfine splitting pattern whose parameters (at 295 K, H = 128±5 kOe, δ = 0.2±0.1 mm s^{-1}, ε_Q = +0.06±0.04 mm s^{-1}) are in good agreement with those reported for Sn^{4+} ions in a similar sample obtained using aqueous ammonia.[3] Thus, the use of hydrazine hydrate affected neither the valence state of the tin dopant nor its distribution in the material.

The ^{57}Fe spectrum of sample B at 295 K [Figure 2(*a*)] consists of a magnetic sextet with H = 510 kOe and a quadrupole-split centre line. The former spectral component corresponds to crystalline α-Fe_2O_3, and the latter, to smaller ferric oxide crystallites showing the superparamagnetic behaviour.[2] The ^{119}Sn spectrum [Figure 2(*b*)] consists of only a non-magnetic component.

The ^{57}Fe spectrum at 80 K [Figure 2(*c*)] corresponds to a pure antiferromagnet. This means that the superparamagnetic relaxation time in smaller ferric oxide crystallites became sufficient for producing a magnetically split pattern. In the ^{119}Sn spectrum [Figure 2(*d*)] a diffuse magnetic hyperfine contribution clearly appears, which implies the spin polarization, unequal in strength, of a considerable part of Sn^{4+} ions. Thus, the ions concerned cannot be considered as isolated from α-Fe_2O_3 crystallites.

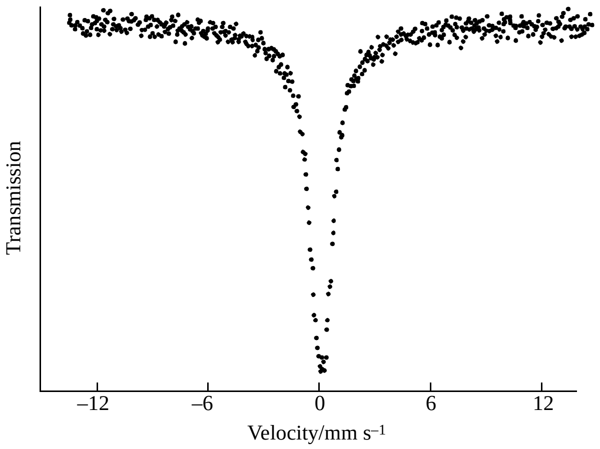

Figure 3 ^{119}Sn spectrum (80 K) of sample B annealed at 700 °C for 24 h.

A more detailed comparison of the data provided by ^{57}Fe and ^{119}Sn probes at 80 K allowed us to conclude that approximately two thirds the tin are spin-polarised with a third present as SnO_2-like non-magnetic clusters, whereas the total Fe^{3+} ions appear in a magnetically ordered state. This points to the partial segregation of the SnO_2 constituent around the smallest α-Fe_2O_3 crystallites. In fact, the high specific surface area of such tin-covered crystallites ($14 > d > 8$ nm; d is the average particle size evaluated on the basis of superparamagnetic relaxation in α-Fe_2O_3 by Kündig *et al.*[2]) allowed us to account for the surprisingly large number of spin-polarized Sn^{4+} ions in sample B (*ca*. 7 at.%) as compared with an upper limit concentration of 1 at.% Sn^{4+} in the α-Fe_2O_3 matrix. Moreover, the location of tin on the available α-Fe_2O_3 surface sites with non-equivalent cationic (magnetically active) surroundings explains the lack of resolution in the magnetically-split component, in contrast with the relevant spectrum in Figure 1.

In sample B, various Fe^{3+}–O–Sn^{4+} exchange contacts can be formed upon the condensation of the material produced by decomposition of metal-containing hydrated species. The occurrence of such links produces SnO_2-like small islands strongly bonded to the surface Fe^{3+} cations. The formation of these tin oxide islands inhibits the growth of α-Fe_2O_3 crystallites. This explains the fact that the magnetic hyperfine fields are transferred towards Sn^{4+} ions from the smallest α-Fe_2O_3 crystallites. Note that the annealing of sample B at 700 °C completely destroyed the Fe^{3+}–O–Sn^{4+} exchange bonds (collapse of the magnetic ^{119}Sn spectral component in Figure 3). This effect is consistent with the low bulk solubility of Sn^{4+}, which leads to rapid saturation of the surface-adjacent layers with tin and precipitation of SnO_2 clusters upon further crystallization of the smallest α-Fe_2O_3 particles. Such a process is obviously different from that reported previously for the samples obtained by mechanically alloying α-Fe_2O_3–SnO_2 ceramics.[9] In this case, the collapse of the magnetic ^{119}Sn spectral component upon annealing the samples could be accounted for by the destruction of metastable ‘solid solution’ domains produced by high energy ball milling;[9] these domains were certainly absent from our sample B.

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